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SYNTHESIS AND PROPERTIES OF  
STEREOREGULAR FLUOROPOLYMERS

by

Patrique Michelle Blackmore, B.Sc. (Hons.)  
(Graduate Society)

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A thesis submitted  
for the Degree of Doctor of Philosophy  
to the University of Durham.

1986



15. FEB. 1987

To Andrew

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First and foremost, I would like to thank Dr. W.J. Feast for his help, encouragement and support throughout my stay in Durham.

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Finally, thanks go to Andrew for his help and encouragement.

MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Laboratories of the University of Durham between September 1983 and August 1986. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

Parts of this work have been the subject of the following publications:

- (i) A.B. Alimuniar, P.M. Blackmore, J.H. Edwards, W.J. Feast and B. Wilson, Polymer, 27, 1281, 1986;
- (ii) P.M. Blackmore and W.J. Feast, Polymer, 27, 1206, 1986;
- (iii) P.M. Blackmore and W.J. Feast, J.Mol.Cat., 36, 145, 1986; and
- (iv) P.M. Blackmore, W.J. Feast and P.C. Taylor, submitted for publication to Br.Polym.J.

Aspects of the work have also been presented, as posters, by the author at the following meetings:

- (i) General Poster Meeting, University of Newcastle-upon-Tyne, December, 1985;
- (ii) 'Tailor Made Polymers', University of Lancaster, March, 1986;
- (iii) 'Centenary of the Discovery of Fluorine', Paris, August, 1986.

SYNTHESIS AND PROPERTIES OF  
STEREOREGULAR FLUOROPOLYMERS

by  
PATRIQUE M. BLACKMORE

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ABSTRACT

The work described in this thesis was concerned with the synthesis and metathesis ring opening polymerization of some fluorinated norbornenes and norbornadienes. The objectives of the work were to synthesise some new stereoregular fluoropolymers.

This thesis is divided into five chapters. In the first chapter the background of the olefin metathesis reaction is reviewed. Chapter Two gives details of the synthesis of some fluorinated norbornenes and norbornadienes. The third chapter discusses the ring opening metathesis polymerization of a series of relatively simple monomers, and the characterization of the polymers produced, by  $^{13}\text{C}$  n.m.r. and infrared spectroscopy. In the fourth chapter the polymerization of a series of more complicated monomers is described. The final chapter details some of the physical properties of the polymers.

<u>CONTENTS</u>	<u>Page No.</u>
Acknowledgements	i
Memorandum	ii
Abstract	iii
<u>CHAPTER ONE - INTRODUCTION</u>	1
1.1 General Introduction	2
1.2 Polymer Classification	2
1.3 Definition of the Olefin Metathesis Reaction	3
1.4 Catalyst Systems	4
1.5 Thermodynamics of the Olefin Metathesis Reaction	6
1.6 Mechanism of the Olefin Metathesis Reaction	8
(a) Transalkylation or transalkylidenation	8
(b) Initiation	9
(c) Propagation	13
(d) Termination	16
1.(i) Chain transfer between Propagating Species and Polymer Chains	16
(ii) Chain Transfer between the polymer chain and an acyclic alkene	17
2. Back biting and the Formation of Cyclic Oligomers	17
3.(i) Termination by Reaction of a Metallocarbene	18
1.7 Range of Monomers Susceptible to Olefin Metathesis	19
(a) Acyclic Olefins	19
(b) Cyclic Olefins	20
1.8 Microstructure of Polymer Chains and Stereoregularity	22
(a) Stereoregularity	22
(i) <i>Cis/trans</i> double bonds	23
(ii) Head/tail effects	23
(iii) Tacticity Effects	24
1.9 Stereoregularity and the Olefin Metathesis Reaction	27
(a) Formation of <i>cis</i> or <i>trans</i> double bonds	27
(b) Tacticity effects	29
(c) Head/Tail Bias in Polymer Chains	30

	<u>Page No.</u>
1.10 Blockiness in polymer chains	34
1.11 The Reactive face in Norbornene derivatives	36
1.12 Application of the Olefin Metathesis Reaction to the Synthesis of Stereoregular Fluoropolymers	37
1.13 Range and Uses of Some Common Fluoropolymers	38
(a) Fluorine in Organic Chemistry	38
(b) <u>Some Common Fluoropolymers</u>	38
(i) Poly(tetrafluoroethylene)	38
(ii) Poly(vinylidene fluoride)	39
(iii) Poly(vinyl fluoride)	40
(iv) Poly(chlorotrifluoroethylene)	40
(v) Difluoroethylene-hexafluoropropene Copolymer	40
(vi) Nafion Membranes	40
(c) Conclusions	41
1.14 Stereoregulation in Polymer Chains and property dependence	41
1.15 Stereoregular Fluoropolymers	42
(a) General	42
(b) Specific Work on Stereoregular Fluoropolymers	43
(c) Conclusions	44
1.16 Objectives of the Work described in this thesis	45
<u>CHAPTER TWO - SYNTHESIS AND CHARACTERIZATION OF MONOMERS</u>	47
2.1 The Diels Alder Reaction	48
2.2 Synthesis and Characterization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (I)	50
2.3 Synthesis and Characterization of 2-trifluoromethyl-bicyclo[2.2.1]hepta-2,5-diene (II)	52
2.4 Synthesis and Characterization of Exo and Endo 5-trifluoromethyl bicyclo[2.2.1]hept-2-ene (III and IV)	53
2.5 Attempted Alternative Synthesis of Endo 5-trifluoromethyl bicyclo[2.2.1]hept-2-ene	55
2.6 Synthesis and characterization of 5-(2'-bromotetrafluoroethyl bicyclo[2.2.1]hept-2-ene (V)	58
2.7 Synthesis and Characterization of 5-pentafluorophenyl bicyclo[2.2.1]hept-2-ene (VI)	62



2.8	(a)	Synthesis and Characterization of <i>exo</i> - <i>N</i> -pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (VII)	66
	(b)	Synthesis and Characterization of <i>endo</i> - <i>N</i> -pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (VIII)	68
2.9		Synthesis and Characterization of 5-perfluorohexyl bicyclo[2.2.1]hept-2-ene (IX)	72
2.10		Synthesis and Characterization of 5-perfluorooctyl bicyclo[2.2.1]hept-2-ene (X)	75
EXPERIMENTAL -			78
2.11	(a)	Reagents	79
	(b)	Preparation of 3,3,3-trifluoropropyne	79
	(c)	Reaction of Cyclopentadiene with a fluoroalkene or fluoroalkyne	80
	(i)	General Procedure	80
	(ii)	2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (I)	80
	(iii)	2-Trifluoromethyl bicyclo[2.2.1]hepta-2,5-diene (II)	81
	(iv)	Exo and Endo-5-trifluoromethyl bicyclo[2.2.1]hept-2-ene	81
	(v)	5-Pentafluorophenyl bicyclo[2.2.1]hept-2-ene	81
	(vi)	5-(2-Bromotetrafluoroethyl) bicyclo[2.2.1]hept-2-ene	82
	(vii)	5-Perfluorohexyl bicyclo[2.2.1]hept-2-ene	82
	(viii)	5-Perfluorooctyl bicyclo[2.2.1]hept-2-ene	82
	(d)	Synthesis of Exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride	83
	(e)	Synthesis of Endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride	83
	(f)	Synthesis of <i>exo</i> - <i>N</i> -pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (VII)	84
	(g)	Synthesis of <i>endo</i> - <i>N</i> -pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (VIII)	84
	(h)	Attempted Synthesis of Endo-5-trifluoromethyl bicyclo[2.2.1]hept-2-ene	85
	(i)	Synthesis of 5-carboxyl bicyclo[2.2.1]hept-2-ene	85
	(ii)	Synthesis of the iodolactone of 5-carboxynorbornene	85
	(iii)	Attempted fluorination of 5-carboxy bicyclo[2.2.1]hept-2-ene	86

CHAPTER THREE - POLYMERIZATION OF 2,3-BIS(TRIFLUOROMETHYL)NORBORNADIENE, 2-TRIFLUOROMETHYLNORBORNADIENE, AND EXO AND ENDO-5-TRIFLUOROMETHYLNORBORNENE	87
3.1 Nomenclature	88
3.2 Background	88
3.3 Analytical Methods	89
(a) Infrared spectroscopy	89
(b) Nuclear Magnetic Resonance Spectroscopy	89
(i) <i>Cis/trans</i> double bonds	90
(ii) Head/tail effects	92
(iii) Meso/racemic effects	92
3.4 Polymerization of 2,3-bis(trifluoromethyl)-nornbornadiene(I)	93
(a) Interpretation of the $^{13}\text{C}$ n.m.r. spectrum	93
(b) Catalysts Effecting the polymerization of (I)	96
(c) Polymerization of (I) using $\text{MoCl}_5/\text{Me}_4\text{Sn}$	103
(d) Infrared spectra of Polymers of (I)	106
3.5 Polymerization of 2-trifluoromethylnornbornadiene(II)	110
(a) Catalysts Effecting the Polymerization of (II)	110
(b) Infrared spectra of polymers of (II)	112
(c) $^{13}\text{C}$ n.m.r. spectra of polymers of (II)	112
3.6 Polymerization of endo (III) and exo (IV) 5-trifluoromethylnornbornene	120
(a) Catalysts effecting the polymerization of (III) and (IV)	120
(b) Infrared Spectra	121
(c) $^{13}\text{C}$ N.m.r. of Polymers of exo and endo-5-trifluoromethylnornbornene	123
3.7 Conclusions	138
EXPERIMENTAL -	139
3.8 Polymerizations	140
(a) Reagents	140
(b) Polymerization procedure	140
(c) Purification of polymers	142

<u>CHAPTER FOUR</u> · <u>METATHESIS POLYMERIZATION OF A RANGE OF FLUORINATED NORBORNENE DERIVATIVES</u>	144
4.1 Introduction	145
4.2 Polymerization of 5-bromotetrafluoroethyl-norbornene (V)	145
(a) Catalysts effecting the polymerization of (V)	145
(b) Infrared spectra of polymers of (V)	146
(c) <sup>13</sup> C N.m.r. spectra of polymers of (V)	146
4.3 Polymerization of 5-pentafluorophenyl-norbornene (VI)	155
(a) Catalysts	155
(b) Infrared spectra of polymers of (VI)	156
(c) <sup>13</sup> C N.m.r. spectra of Polymers of (VI)	156
4.4 Polymerization of exo(VII) and endo(VIII)-pentafluorophenyl-2,3-dicarboximidenorbornene	160
(a) General	160
(b) Infrared spectra of polymers of N-pentafluorophenyl-2,3-dicarboximide norbornene	161
(c) <sup>13</sup> C N.m.r. spectra of polymers of N-pentafluorophenyl-2,3-dicarboximide norbornene	161
4.5 Polymerization of 5-perfluorohexylnorbornene (IX)	170
4.6 Polymerization of 5-perfluorooctylnorbornene (X)	171
4.7 Gel permeation chromatography and molecular weight distribution	172
4.8 Conclusions	173
EXPERIMENTAL -	
4.9 Reagents	175
4.10 Polymerization procedure	175
<u>CHAPTER FIVE</u> - <u>PHYSICAL PROPERTIES OF SOME FLUORINATED POLY(NORBORNENES) AND POLY(NORBORNADIENES)</u>	176
5.1 Introduction	177
5.2 Differential Scanning Calorimetry	177
5.3 Thermogravimetric Analysis	183
5.4 Conclusions	186

	<u>Page No.</u>
<u>CHAPTER SIX</u> ·· <u>CONCLUSIONS AND PROPOSALS FOR</u> <u>FURTHER WORK</u>	187
APPENDIX A ·· APPARATUS AND INSTRUMENTS	191
APPENDIX B ·· INFRARED SPECTRA	192
APPENDIX C ·· MASS SPECTRA	201
REFERENCES	204

CHAPTER ONE

INTRODUCTION



### 1.1 General Introduction

Despite the importance of both synthetic and naturally occurring polymers to man, an understanding of the science of high polymers has begun to emerge only relatively recently. In the early years of this century scientists believed that materials such as cellulose and rubber were colloidal aggregates. Staudinger<sup>1</sup> challenged this idea and his work forced scientists to accept the concept that these molecules were built up by the repetition of small structural subunits (monomers), to form long chains or macromolecules. By the middle of the twentieth century the discovery and utilization of, for example, nylon, perspex, polystyrene and poly(vinylchloride) caused an avalanche of activity in the area of polymer science, as a result of which knowledge was greatly expanded. This process of invention, study and increasing understanding continues to the present day.

### 1.2 Polymer Classification

Classically W.H. Carothers<sup>2</sup> divided polymerization reactions up into two types; addition and condensation. This classification had several drawbacks<sup>3</sup> and it is now more appropriate to describe polymerization reactions on the basis by which the chain grows: either

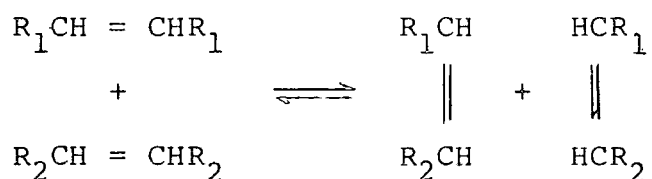
- (i) chain growth polymerization, or
- (ii) step growth.

The synthetic method of polymerization described in this thesis is the olefin metathesis reaction, an unusual type of chain growth polymerization.

### 1.3 Definition of the Olefin Metathesis reaction

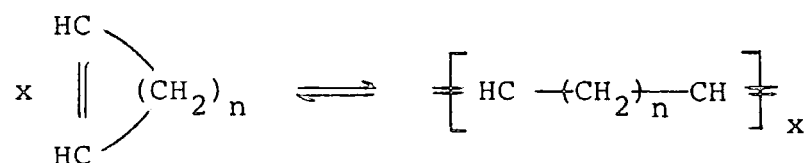
The olefin metathesis reaction is a catalytically induced bond reorganization process involving the making and breaking of carbon-carbon double bonds. During the process the number and type of bonds remains unchanged.

For acyclic olefins the overall process leads to exchange of alkylidene units.



This reaction was discovered by Banks and Bailey,<sup>4</sup> who termed the reaction "olefin disproportionation".

For cyclic olefins the metathesis reaction leads to ring opening and the formation of linear polymers.



The first citation of ring opening polymerization of alkenes was given in a patent by Eleuterio<sup>5</sup> in 1957, and later reported in the open literature by Truett.<sup>6</sup> It was not until the work of Calderon<sup>7</sup> in 1967, that it was realised that ring opening polymerization of alkenes to yield unsaturated polymers and the olefin disproportionation reaction were governed by the same mechanism, and the term olefin metathesis was introduced to describe both of these reactions.

The olefin metathesis reaction has been extensively reviewed and is the subject of recent books.<sup>8,9a,b</sup> A detailed

description of the reaction is therefore unnecessary, and an outline of salient features and recent developments in the metathesis of cyclic olefins, relevant to the work to be described in this thesis, will be given in this brief review.

#### 1.4 Catalyst Systems

The olefin metathesis reaction is catalytically induced, and the range of catalysts which will initiate the reaction is very large.<sup>10</sup> They consist of compounds of the transition metals from groups IVA to VIII as shown in Figure 1.1

IVA	VA	VIA	VIIA	VIII
Ti	V	Cr		
Zr	Nb	Mo		Ru Rh
Hf	Ta	W	Re	Os Ir

FIGURE 1.1 Metals active in the catalysis of metathesis

-----

Catalyst systems consist of three main types:

- (i) single component systems comprised of a metal carbene;
- (ii) two component systems containing a transition metal compound and an alkyl, aryl or allyl containing species;
- (iii) compounds with neither a preformed carbene or an alkyl, aryl or allyl containing species, and usually consisting of a transition metal halide.



The number of catalysts which will initiate a particular metathesis process is governed to some extent, by the magnitude of the free energy change. Reactions with large negative  $\Delta G$  values will, in general, be initiated by a larger range of catalyst systems than reactions with small  $\Delta G$  values.

The ratio of *cis* and *trans* double bonds in a ring opened polymer is primarily dependent on the catalyst, but other parameters such as concentration, temperature and the nature of the monomer can also have an influence. In this work catalysts based on W, Mo, Re, Os, Ru and Ir have been used, and in general, it seems that W and Mo based catalysts are more reactive than those based on the other transition metals. The selectivity of W and Mo based catalysts is variable whereas the other systems seem to be more specific; thus,  $\text{ReCl}_5$  gives ring opened polymers with a high *cis* vinylene content, whereas  $\text{OsCl}_3$ ,  $\text{RuCl}_3$  and  $\text{IrCl}_3$  all tend to give high *trans* products. It has to be admitted that most studies reported to date have concentrated on W or Mo based catalysts, and consequently there is much more data about these systems. It may well be that the generalisations about Re, Os, Ru and Ir based catalysts will not stand the test of time. Indeed, a recent report<sup>11</sup> concerning the polymerization of endo-dicyclopentadiene with  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  catalyst describes an unusual result. For a wide range of substituted norbornenes, including exo-dicyclopentadiene,  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  gives rise to a high *trans* polymer, whereas with endo-dicyclopentadiene a high *cis* polymer is obtained. This observation was rationalised in terms of propagation by a sterically restricted catalyst in which endo-dicyclopentadiene acts as a bidentate ligand. The resulting

increase in steric bulk forces the monomer to approach in such a way that a *cis* double bond is formed.

### 1.5 Thermodynamics of the Olefin Metathesis Reaction

For any reaction the change in Gibbs free energy has to be negative for the process to be favourable.

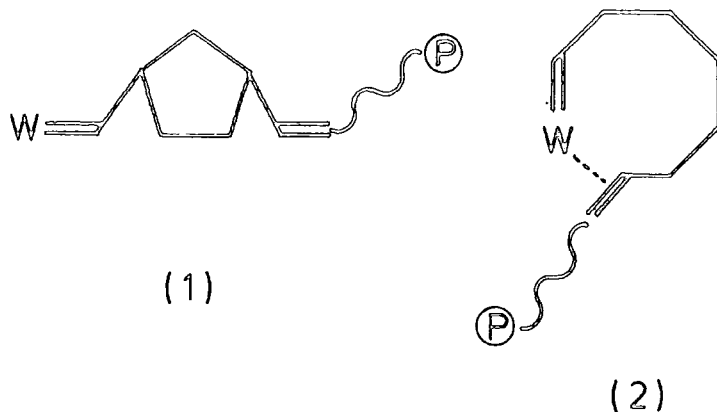
$$\Delta G = \Delta H - T\Delta S$$

The entropy term for polymerization reactions is always negative since the freedom of the monomers has been constrained by binding them into macromolecules. Consequently, the second term in the expression for  $\Delta G$  is always positive. Successful reaction requires that the enthalpy change ( $\Delta H$ ) outweighs the  $T\Delta S$  term. It has been observed that there is a temperature, characteristic of the monomer, above which polymerization cannot be achieved. This "ceiling temperature" effect is readily understood in terms of the above considerations.<sup>12</sup> If the temperature is too high then the overall  $\Delta G$  becomes positive and the process unfavourable. The temperature at which the  $T\Delta S$  term balances the  $\Delta H$  term defines the "ceiling temperature".

It seems reasonable to expect that the most important factor in determining the  $\Delta G$  value for a ring opening process will be ring strain. The experimental evidence supports this view; thus small membered rings are easily polymerized, but cyclohexene in which there is no ring strain has so far proved extremely resistant to attempts to polymerize it.

However, there is a report in the literature which questions this argument.<sup>13</sup> It is claimed that ring strain is not

the most important feature in explaining the different reactivities of cyclic olefins towards metathesis catalysts. These workers propose that it is the relative reactivity of the propagating carbene (see Section 1.6) that is crucial. The rates of reaction of norbornene and cyclooctene, in the presence of tungsten hexachloride/tetramethyltin catalyst system, were measured; and it was determined that norbornene was polymerized faster by a factor of  $10^2$ . This was rationalized in terms of the relative reactivity of the chain carrying species for norbornene (1) and cyclooctene (2).



It was suggested that the vinylenes in the polymer chain in (1) could not coordinate to the metal centre, whereas in (2) co-ordination could take place, as shown above. The tungsten carbene in (1) has a "free active site" which is therefore more reactive than that in (2), where the active site is shielded by an 'in chain' vinylene. Arguments about coordinated vinylenes have been advanced previously to account for observed tacticity effects (see later). It seems that the distinction envisaged by these authors is somewhat tenuous, since in the polymerization mechanism the in-chain vinylene is produced as a result of cleaving a metallocyclobutane and,

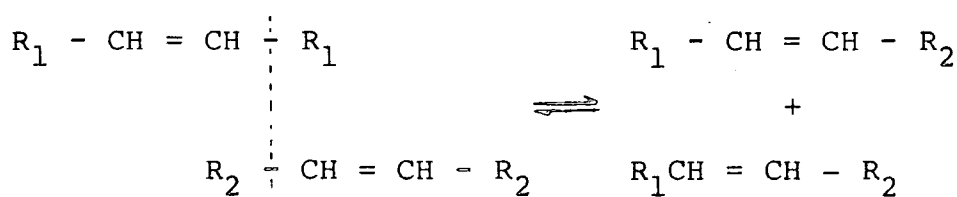
at the moment of its formation, it must be in very close proximity to the newly formed active site and metal carbene. Whether it stays coordinated to the active site influencing the approach of incoming monomer (and thereby affecting both tacticity and reactivity) or rapidly becomes decoordinated, would be expected to be a function of strain in the system. Thus, it seems that the established view of the dominance of ring strain is not seriously challenged by this recent publication.

## 1.6 Mechanism of the Olefin Metathesis Reaction

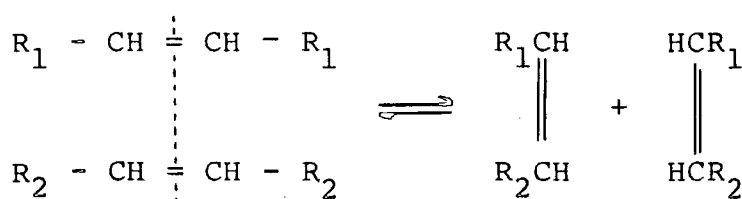
### (a) Transalkylation or transalkylidenation

The currently accepted mechanism for the olefin metathesis reaction is one involving a carbene as chain carrier.

Initially two interchange processes, transalkylation<sup>14</sup> and transalkylidenation were postulated as possible routes, as illustrated in Figure 1.2.



TRANSALKYLATION



TRANSALKYLIDENATION

FIGURE 1.2 Transalkylation and transalkylidenation as possible pathways for the metathesis reaction

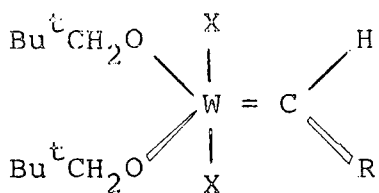
A transalkylidenation scheme was proved by  $^{14}\text{C}$  and deuterium labelling experiments.<sup>15-18</sup> Further confirmation that cleavage was occurring at the double bond itself, came from copolymerizing cyclooctene and labelled cyclopentene, followed by ozonolysis and reductive cleavage.<sup>19,20</sup>

Early mechanisms for the reaction which were consistent with cleavage at the double bond involved quasi-cyclobutane intermediates,<sup>21-23</sup> tetramethylene transition states<sup>24</sup> or metallocyclopentanes,<sup>25,26</sup> all involving a pairwise mechanism. The evidence for a non-pairwise mechanism, first proposed by Herisson and Chauvin,<sup>27</sup> involving a metallocarbene as chain carrier is now overwhelming, and pairwise mechanisms have been abandoned. Olefin metathesis reactions, like other chain processes proceeds *via* initiation, propagation and termination steps, and some of the main evidence for the species involved in each step is given below.

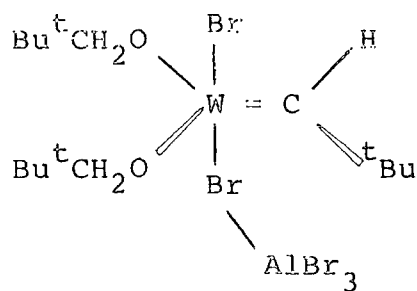
(b) Initiation

The fact that stable metallocarbenes such as the Casey<sup>28-30</sup> and Fischer<sup>31-34</sup> carbenes will induce the olefin metathesis reaction provides good evidence that these species are involved in the initiation step.

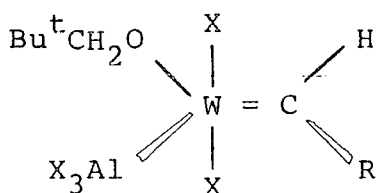
Osborne *et al*<sup>35-37</sup> have synthesized and established the structures of several stable tungsten IV carbenes including (3), which although inactive itself, gave highly active catalyst systems on addition of  $\text{AlBr}_3$ . The active species were shown to be (4) and (5).



(3)



(4)



(5)

In cases where the initiating species is a transition metal compound and an alkyl or allyl containing species, reaction between these components is believed to yield a metallo-carbene compound. Several possible mechanisms by which this may occur are suggested in the literature.<sup>38-43</sup> Two examples are shown in Figure 1.3

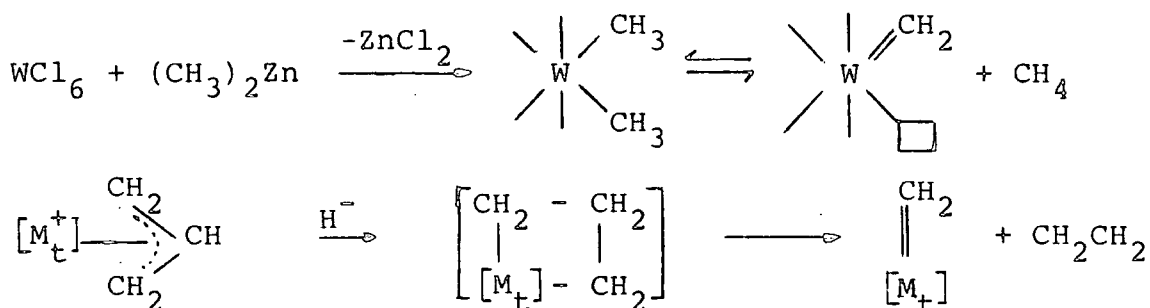


FIGURE 1.3 Postulated metallocarbene formation sequences

Some single component transition metal halides are active in metathesis catalysis, although it may be that trace amounts of oxygen or water in the monomer or reaction vessel serve as a second component involved in the generation of the active species.

In other cases, reaction between the substrate olefin and transition metal compound is believed to result in the form-

ation of a metallocarbene.<sup>44,46</sup> In Figure 1.4 an allylic hydrogen in the coordinated alkene migrates first to the metal centre and then to the central carbon of the resulting  $\eta^3$  allyl ligand, to give a metallocyclobutane, which cleaves to generate the required metallocarbene.

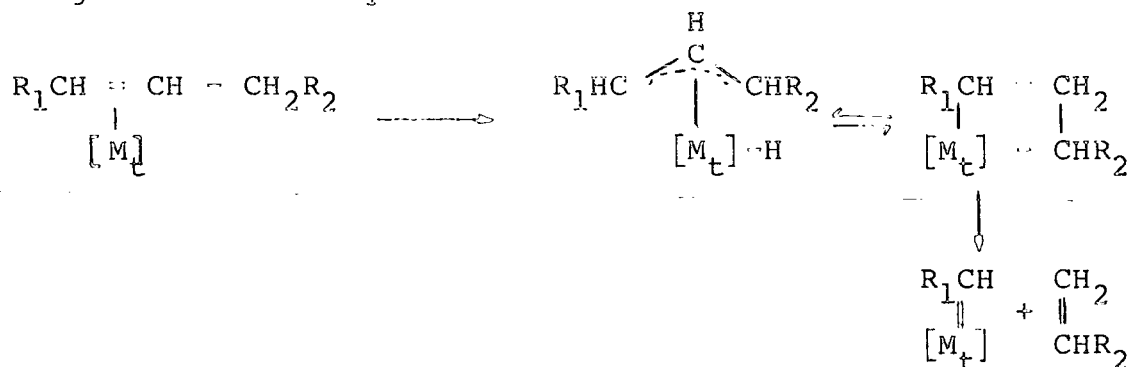


FIGURE 1.4 Possible pathway for the generation of a metallocarbene from a coordinated alkene

Figure 1.5 illustrates a pathway in which a metal hydride bond is generated (a), which then adds to the alkene to give a metal alkyl, which undergoes  $\alpha$ CH bond migration to the metal centre with accompanying formation of a metallocarbene

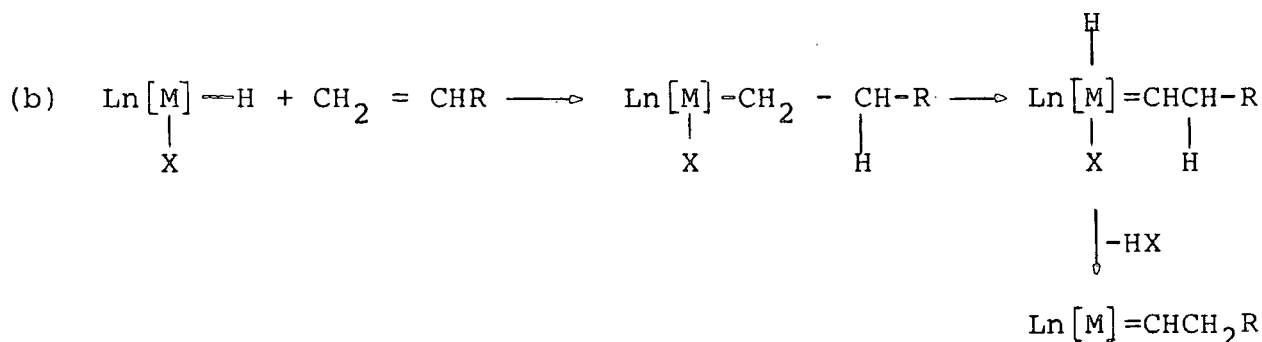
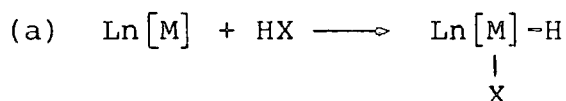
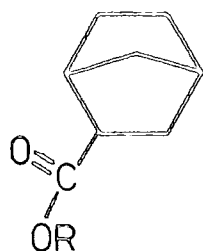


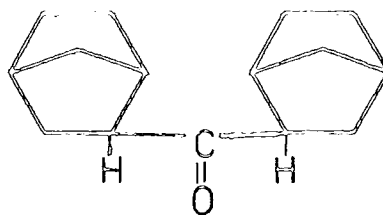
FIGURE 1.5 Possible pathway for the generation of a metallocarbene via initial hydride formation

A recent publication<sup>47</sup> concerning the nature of the initiating species involved in the ring opening polymerization of norbornene using  $\text{W}(\text{CO})_3\text{Cl}_2(\text{AsPh}_3)_2$  as catalyst, constructs

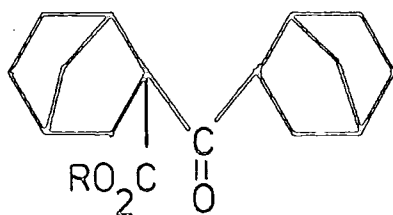
a hypothesis on the basis of the species isolated when the reaction was quenched by ethanol at low conversion. The products present were identified by combined gas chromatography/mass spectroscopy. The major product was the ester (6). Smaller amounts of (7) and (8) were also identified, as well as some 2-chloronorbornane.



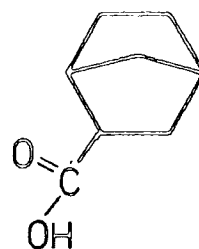
(6)



(7)

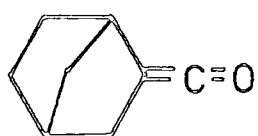


(8)

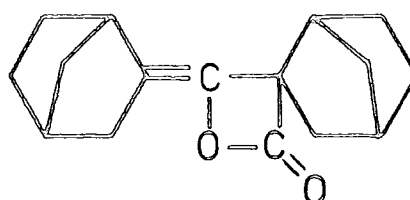


(9)

When water was added to the system ( $H_2O/W$ ) prior to the polymerization, and the reaction subsequently quenched with cold water, the yield of the polymer dropped significantly and increased quantities of (7) and 2-chloronorbornane were identified, while the esters were absent. The ketene (10) and its dimer (11) were suggested to be the most likely precursors for (6)-(9).



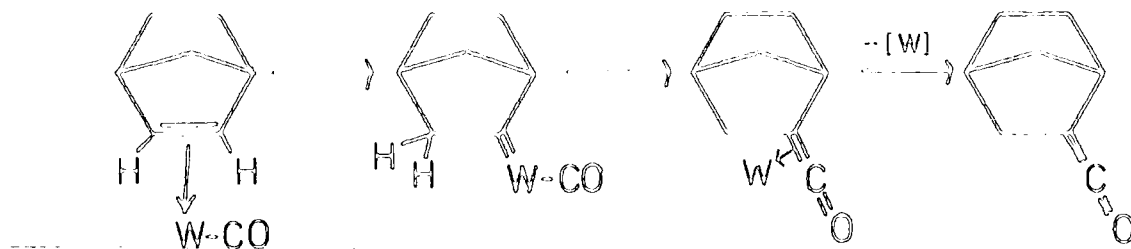
(10)



(11)



It was then envisaged that the ketene was formed *via* the following sequence.



The hydrocarbon part of the initiating carbene is hence formed by a 2,3-hydrogen shift in the coordinated alkene.

(c) Propagation

Propagation takes place *via* reaction of the initiating metallocarbene and olefin leading to the formation of a metallocyclobutane. The metallocycle cleaves regenerating a carbene at the chain end, as shown in Figure 1.6.

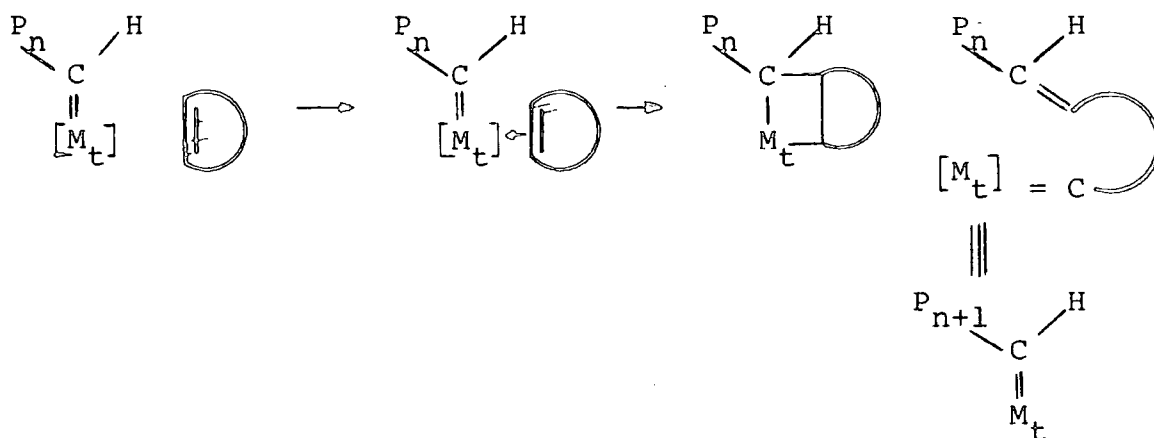


FIGURE 1.6 Outline of the propagation pathway for ring opening metathesis polymerization

Evidence to support the formation of a metallocyclobutane as an intermediate came from the work of Green,<sup>48</sup> who isolated a stable metallocyclobutane, which subsequently gave a metal carbene and alkene on thermolysis or photolysis.

More convincing evidence for this pathway comes from a recent publication by Grubbs and Gillion<sup>49</sup> who have shown that the titanocyclobutanes (12) and (13) (see Figure 1.7), derived from norbornene, will initiate the polymerization of norbornene.

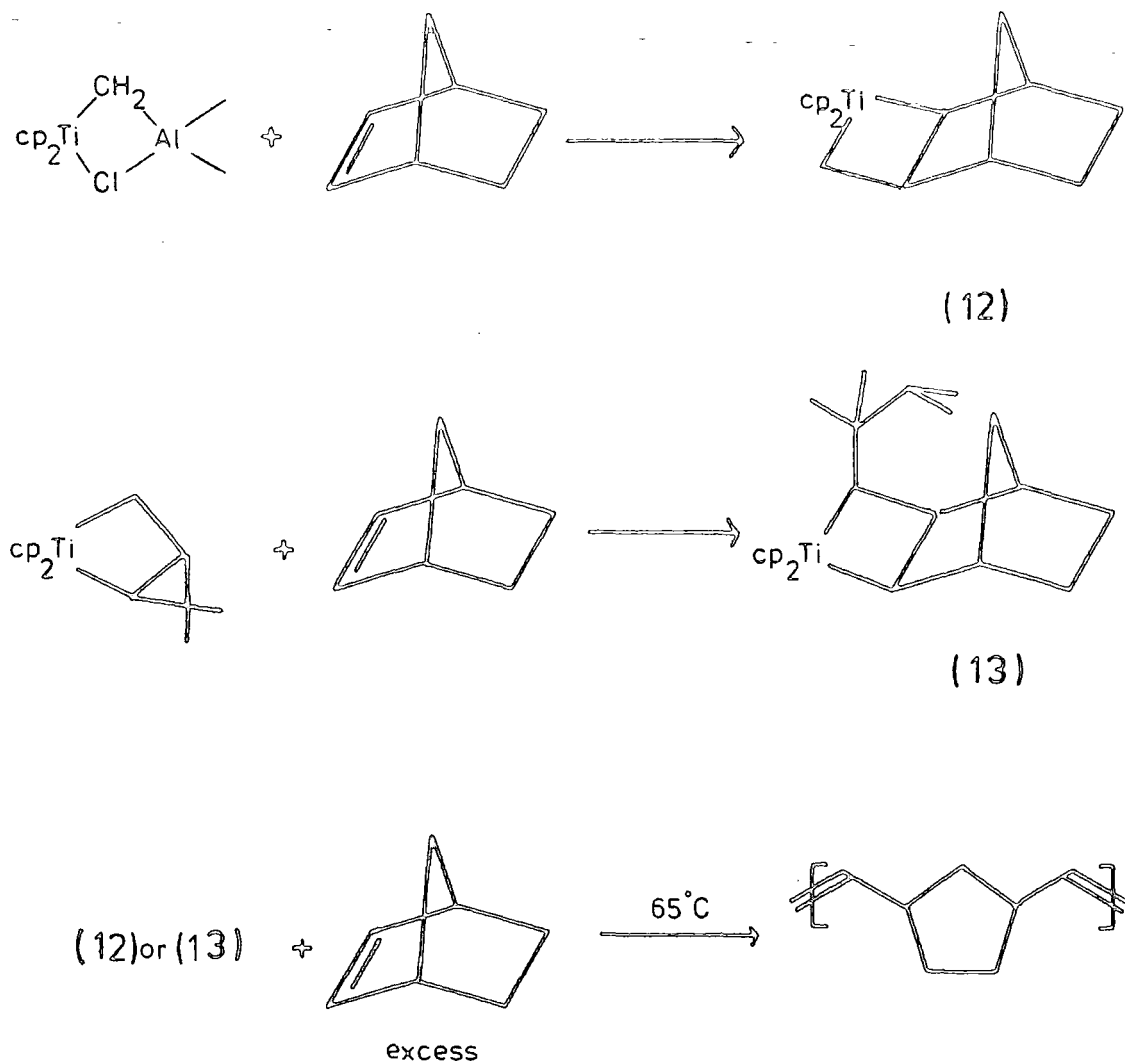


FIGURE 1.7 Examples of isolated metallocyclobutanes

The authors also proved that the catalysts produce "living systems" in the polymerization of norbornene, in which the "living" chain end is a metallocyclobutane.

An alternative mechanism to the currently accepted propagation sequence has been proposed by Rooney.<sup>50</sup> In this modification the consecutive steps of coordination of the olefin to the metal centre followed by formation of a metallocyclobutane, (as shown in Figure 1.6) are replaced by a single cycloaddition step as shown in Figure 1.8.

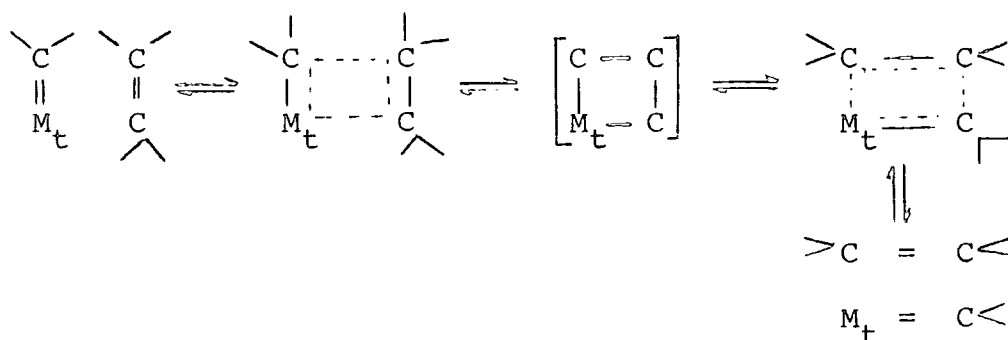


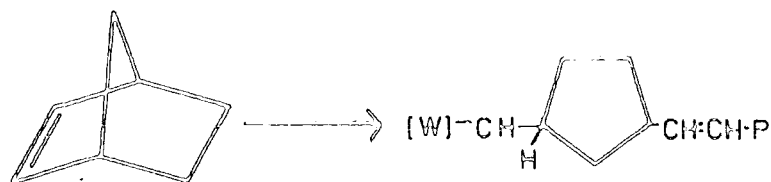
FIGURE 1.8 Alternative mechanism for the propagation step in olefin metathesis

This mechanism was postulated to account for the steric and polar factors which influence the stereospecificity observed in some polymerizations (discussed later, Section 1.9). The scheme has also received support from various theoretical calculations.<sup>51</sup>

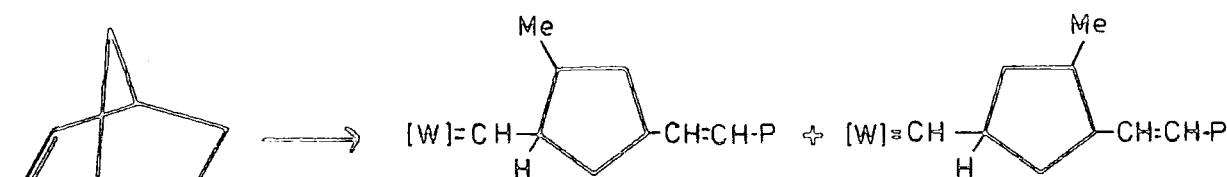
There are two reports of the olefin metathesis reaction occurring in the absence of a transition metal compound. In particular, it was found that norbornene could be ring opened by  $\text{EtAlCl}_2$ .<sup>52,53</sup>

In conjunction with the work of Osborne, Ivin<sup>37</sup> has shown that tungsten carbene complexes initiate the ring opening of some bicyclic alkenes. Using the catalyst system  $\text{W}(\text{CHBu}^t)(\text{OCH}_2\text{Bu}^t)_2\text{Br}_2/\text{GaBr}_3$  several monomers including (14) to (16) were mixed with the catalyst at 240K. The  $^1\text{H}$  nmr

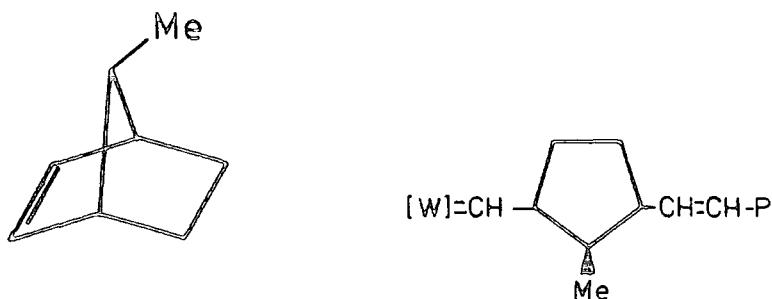
spectra of these samples were recorded and the expected carbene species were identified in each case, (Figure 1.9)



(14)



(15)



(16)

FIGURE 1.9 Some carbene species identified by  $^1\text{H}$  nmr spectroscopy

The authors also prove that these complexes could be described as 'living polymers'.

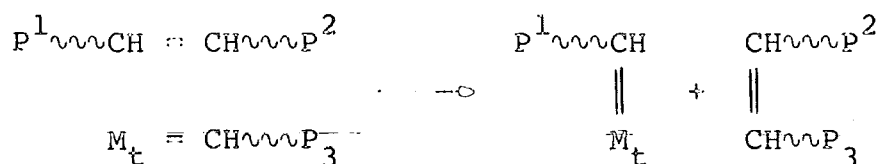
(d) Termination

1. Chain transfer

(i) Chain transfer between Propagating Species and Polymer Chains

Termination of chain growth may take place *via* a

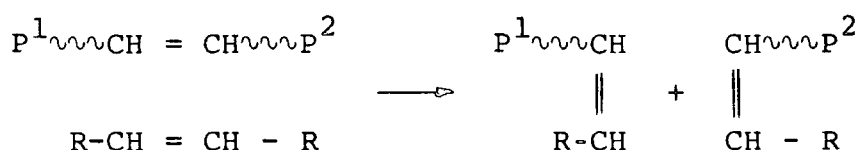
non-productive metathesis reaction between a propagating metallocarbene and carbon-carbon double bond of a newly formed polymer chain, ( $P^1$ ,  $P^2$  and  $P^3$  represent polymer chains).



Although this type of reaction does not destroy active catalyst sites, it effectively reduces their availability for propagation. Monomer and polymer carbon-carbon double bonds compete for active sites, and the greater the conversion of monomer to polymer, the greater the number of catalyst sites involved.

(ii) Chain Transfer between the polymer chain and an acyclic alkene

Addition of an acyclic alkene to a polymerizing system causes a reduction in the molecular weight of the polymer. A cross metathesis reaction occurs between the acyclic olefin and polymer chain.

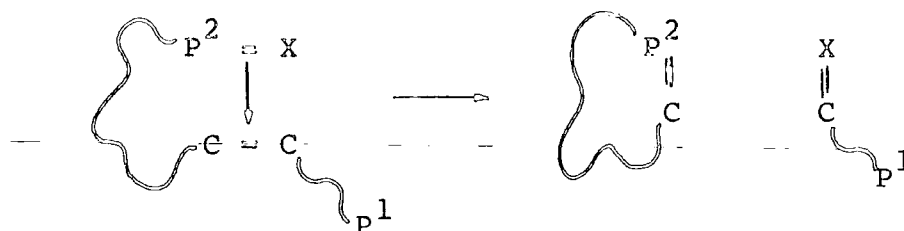


This type of reaction does not destroy active catalyst sites. This reaction can be used to characterize polymers if sufficient acyclic alkene is added and small fragments can be isolated in which, for example, the end groups of the alkylidene moieties can be detected.

2. Back biting and the Formation of Cyclic Oligomers

During the polymerization of cyclic olefins the product

consists of two main fractions; a high molecular weight fraction, and a low molecular weight fraction consisting of cyclic oligomers. Cyclic oligomers are formed *via* an intramolecular backbiting reaction (X = growing chain end)



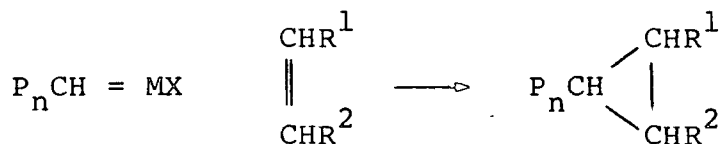
An equilibrium between monomer, high polymer and cyclic oligomer is established. In cases where the initial monomer concentration  $[M_0]$  is below a critical value only cyclic oligomer formation is observed.

### 3. (i) Termination by Reaction of a Metallocarbene

The chain termination reactions described above do not destroy the propagating metallocarbene. Reactions in which the carbene species is destroyed are clearly critical.

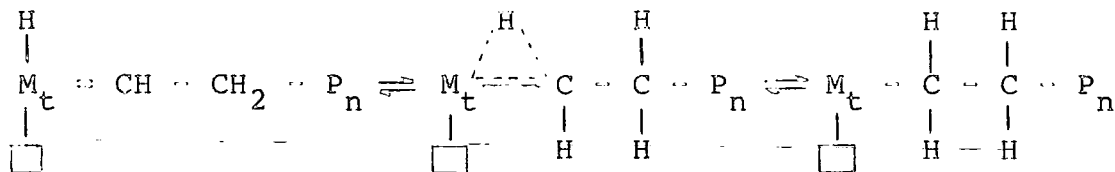
Termination, by proton transfer, can be brought about by the introduction of water or an alcohol. This type of reaction can usually be avoided by modification of experimental procedures.

Termination, by the formation of a cyclopropane seems a feasible possibility. ( $P_n$  represents the polymer chain).

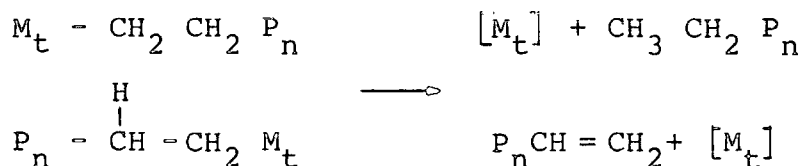


Bimolecular terminations between species that are similar in structure are common in free radical reactions.

In Ziegler Natta such reactions have been proposed to occur *via*  $\beta$ -hydrogen transfer. This can be extended to the metathesis reaction, if it is assumed that the metallocarbene is in equilibrium with a simple transition metal alkyl, as shown below.



Reaction between two metal alkyl species is the effective termination step:



## 1.7 Range of Monomers Susceptible to Olefin Metathesis

### (a) Acyclic Olefins

A list of the acyclic olefins susceptible to olefin metathesis would be long and, in any event, is not the concern of this thesis. Nevertheless it can be said that such metathesis reactions, in which product distributions are statistically determined, can be particularly useful both for the synthesis of materials required in abundance and for low tonnage, highly specialized alkenes.<sup>55-61</sup> The reaction has been used commercially in large scale processes such as the Phillips triolefin process and the Shell FEAST process for producing respectively, ethylene and higher molecular weight

alkenes, and speciality olefins and polyenes. Phillips have also used the process for the synthesis of insect pheromones and perfumery chemicals.<sup>54</sup>

### (b) Cyclic Olefins

The ability of mono- and bicyclic olefins to undergo metathesis depends largely on ring size; for 3,4,8 and larger membered rings metathesis is generally thermodynamically favourable. For 5,6 and 7 membered rings the situation is less clear cut, and the polymerization is sensitive to physical factors such as temperature, monomer concentration and pressure.

Substituents can have a large effect on whether a given cyclic olefin will polymerize. In general only substituents remote from the double bond to be opened can be tolerated. The exception to this rule is when substitution occurs in highly strained rings; thus 1-methyl cyclobutene can be polymerized with ease,<sup>62</sup> Figure 1.10.

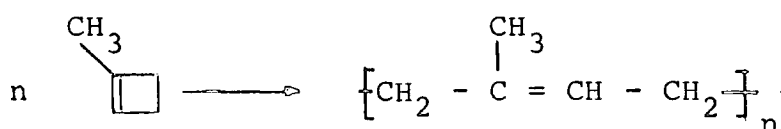


FIGURE 1.10 Ring Opening polymerization of 1-methylcyclobutene

In less strained rings the outcome is less certain, depending to some extent on the amount of strain and the position, nature and size of the substituent. Hence, although 3-methylcyclopentene polymerizes, 3-isopropylcyclopentene will not,<sup>63</sup> neither will 1-methyl cyclopentene.<sup>64</sup>

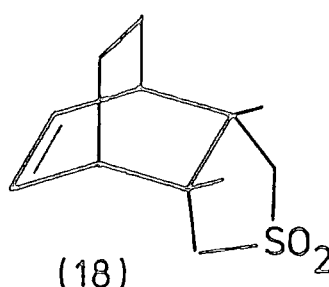
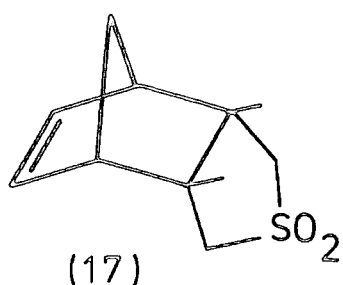
In bicyclo[2.2.1]heptenes methyl substituents are tolerated in all positions; thus Ivin has polymerized methyl



norbornenes substituted at the 1,<sup>65,66</sup> 5<sup>67-69</sup> and 7<sup>70</sup> positions and Katz<sup>71</sup> has reported the polymerization of the 2-substituted isomer.

Heteroatom substitution, in particular, plays a significant role in the outcome of a polymerization; presumably unless the heteroatom is situated sufficiently far away from the double bond, it will destroy the catalyst by occupying the active site on the initiator, since the heteroatom will have donor properties and the active site acceptor properties. A wide range of norbornenes substituted at the 5 and 6 position have been polymerized; thus ester,<sup>72</sup> nitrile,<sup>73</sup> chlorine,<sup>74</sup> fluorine,<sup>75,76</sup> imide,<sup>73</sup> pyridyl,<sup>73</sup> anhydride,<sup>77</sup> carboxyl,<sup>78</sup> amide<sup>79</sup> and carboxylate<sup>80</sup> functionalities can be tolerated by some, but not all, metathesis catalysts.

An alternative explanation to the lack of polymerizability of certain substituted monomers may be given in terms of orbital interactions between a distant group and the olefinic double bond. This type of interaction reduces the electron density on the double bond making co-ordination with a metallo-carbene less favourable. Evidence for this type of interaction comes from the U.V. photoelectron spectroscopy work of Aitken.<sup>81,82</sup> For example, the  $\pi$  electrons of the double bonds in (17) and (18) have ionization potentials which are 0.62eV and 0.75eV higher than those of norbornene and bicyclo[2.2.2]oct-2-ene respectively.



## 1.8 Microstructure of Polymer Chains and Stereoregularity

### (a) Stereoregularity

The physical behaviour of a polymer depends not only on the general composition, but also on subtle differences in microstructure and morphology. It is possible in some cases to tailor make polymers to have the desired microstructure.<sup>83</sup> Not only does this allow one to attempt to design polymers with the required physical properties, but also extends the range of macromolecular species that can be derived from a particular monomer.

The work described in this thesis is concerned with ring opening polymerization of several fluorinated norbornene derivatives as shown in Figure 1.11.

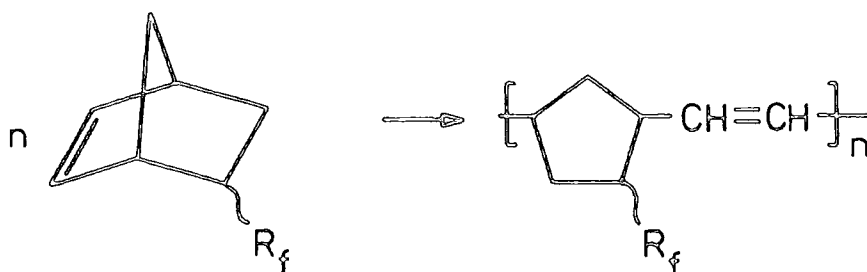


FIGURE 1.11 Generalised case for the ring opening polymerization of a fluorinated norbornene derivative

For this generalised case there can be variations in the abundance and distribution of three features of microstructure of the polymer:

- (i) *Cis* and *trans* double bonds,
- (ii) head, tail effects,
- (iii) and tacticity effects.

(i) Cis/trans double bonds

The metathesis ring opened polymer of norbornene is unsaturated, and the double bonds along the chain may have *cis(c)* or *trans(t)* geometry, as shown in Figure 1.12; the carbon-carbon bonds from the cyclopentane ring to the vinylene are of course 1,3-*cis* disposed on each ring.

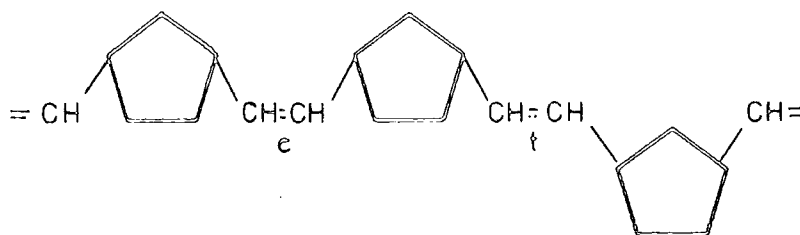
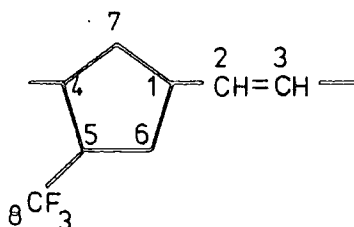


FIGURE 1.12 Cis and trans double bonds in poly(norbornene)

(ii) Head/tail effects

If the monomer is unsymmetrically substituted head/tail effects may be introduced into the polymer chain. Consider, for example, the polymer of 5-trifluoromethyl norbornene, for which the repeat unit and numbering system is shown below.



By definition the portion of the repeat unit substituted with the  $\text{CF}_3$  group (*i.e.* carbons 3,4,5 and 8) is called the head (H) fragment, and the other portion (carbons 1,2 and 6) is defined as the tail (T). This leads to the environment of the

head portion being HH or HT depending on the configuration of the adjacent unit; similarly TT or TH environments are created for the tail part of the repeat unit. This effect is illustrated in Figure 1.13.

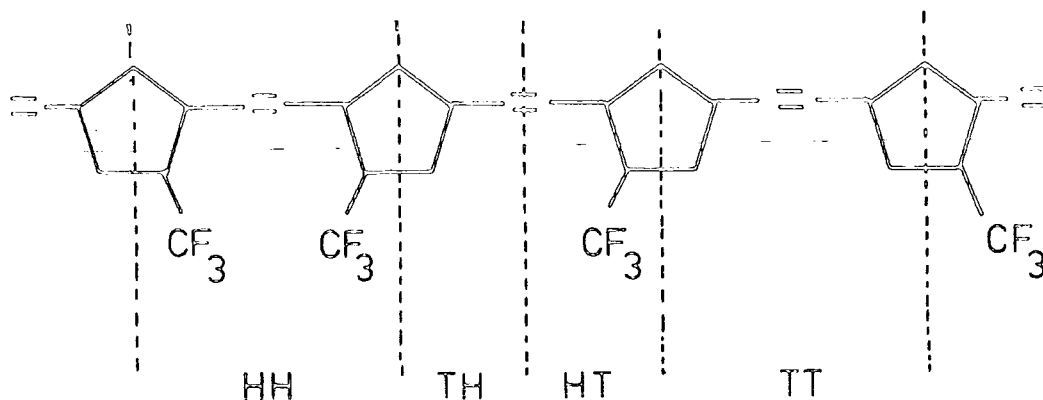


FIGURE 1.13 Head/tail effects in poly(5-trifluoromethyl norbornene)

### (iii) Tacticity Effects

The allylic carbons in polynorbornenes are chiral giving rise to the possibility of having centres on either side of the vinylene unit with the same or opposite chiralities. When the chiralities are the same we have a racemic(r) dyad and sequences of r dyads define a syndiotactic polymer; when the chiralities are opposite we have a meso(m) dyads and sequences of m dyads define an isotactic polymer. An atactic polymer is derived from a random distribution of m and r dyads along the polymer chain. These definitions are illustrated in Figures 1.14 and 1.15 for all *cis* and all *trans* polymers of norbornene.

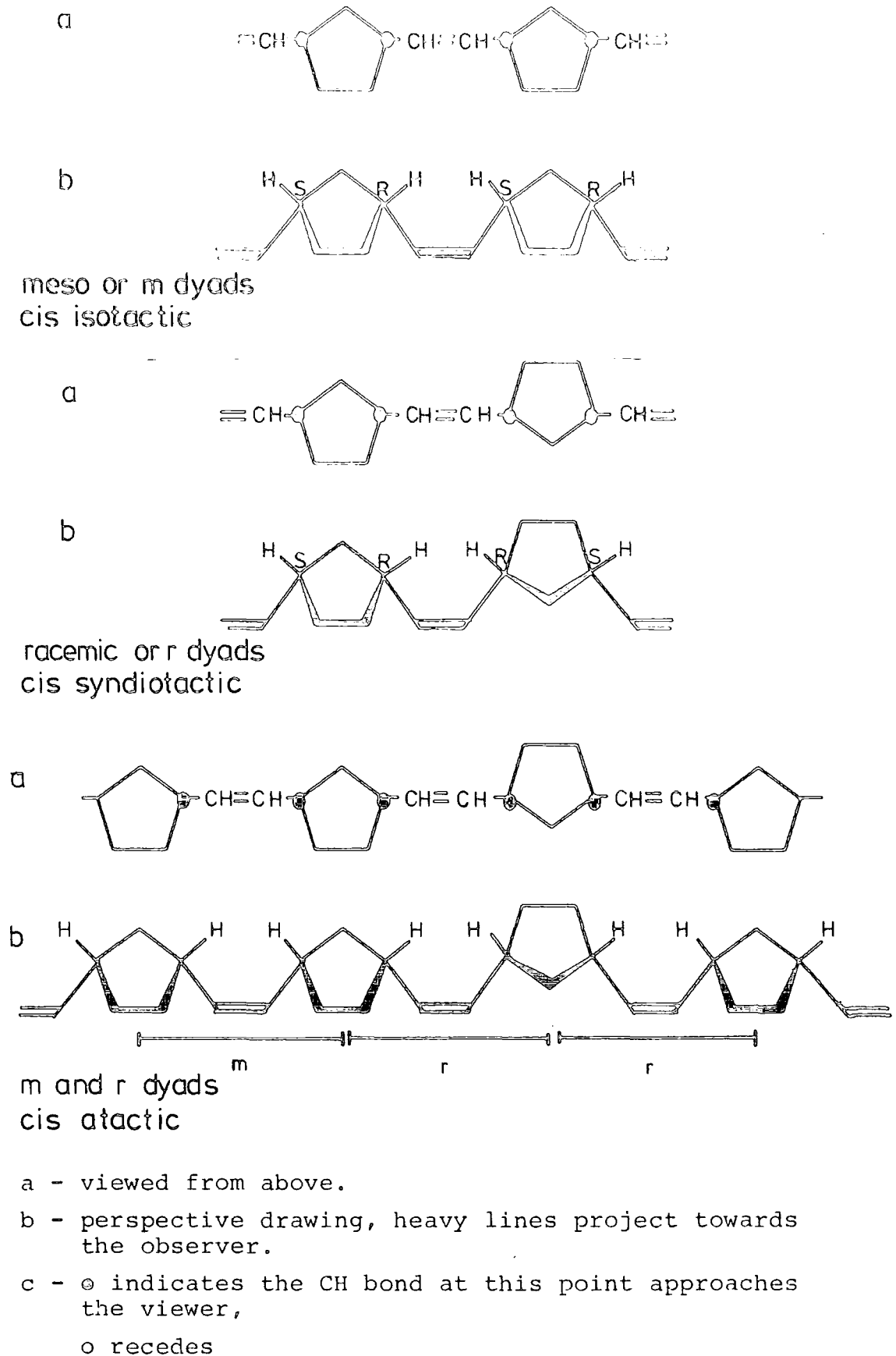
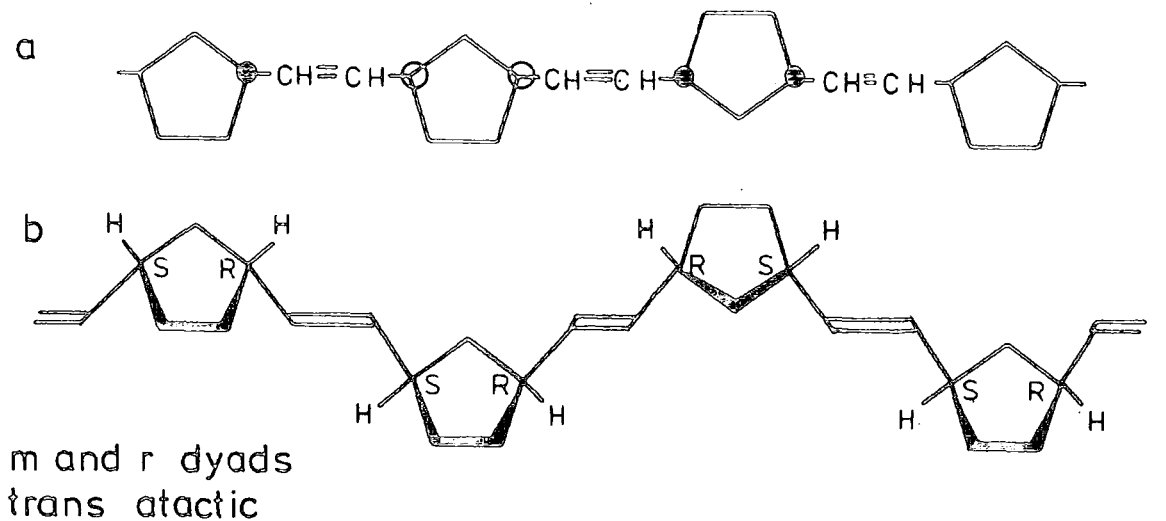
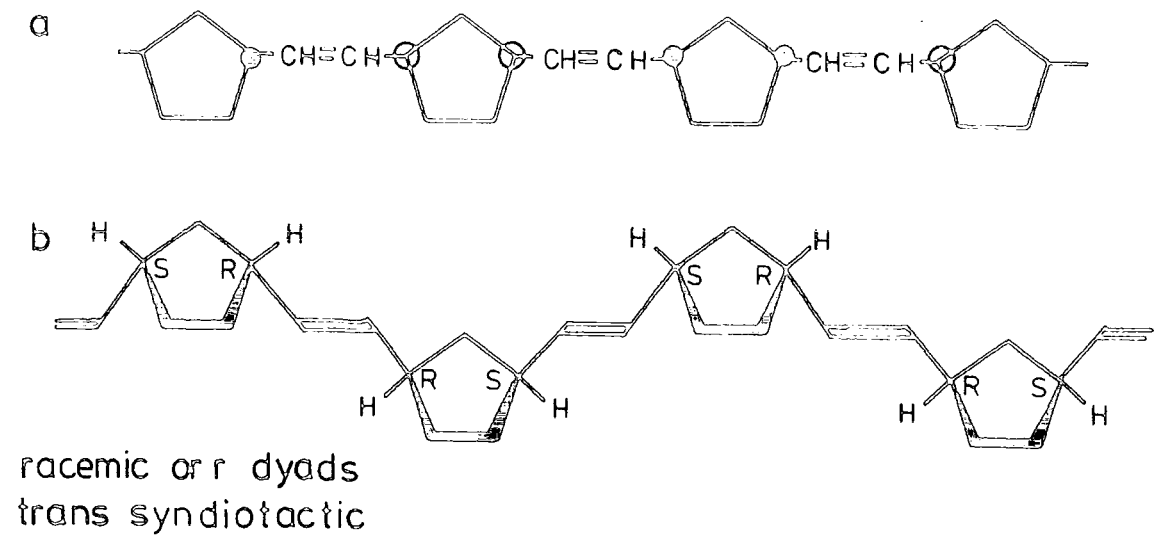
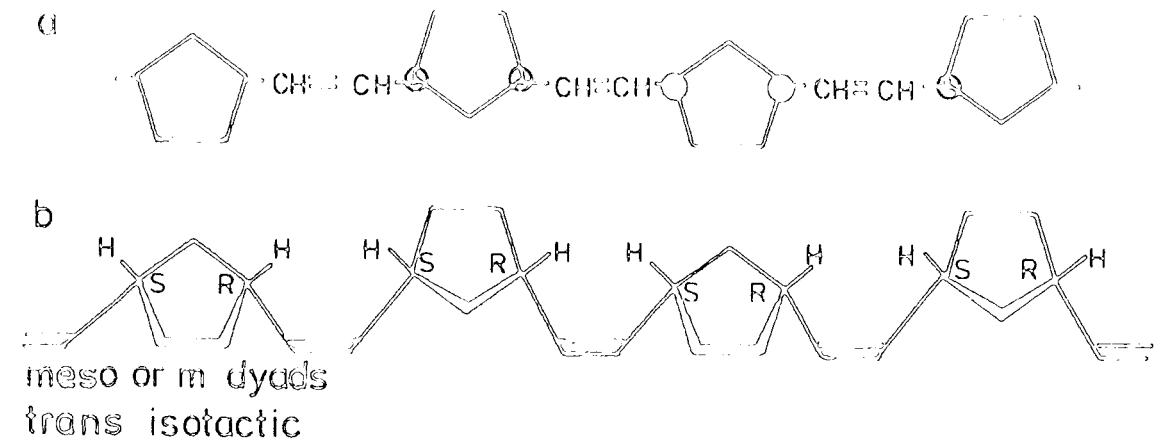


FIGURE 1.14 Tacticity of poly(norbornene)



a - viewed from above.

b - perspective drawing, heavy lines project towards the viewer.

c - o indicates the CH bond at this point approaches the viewer.

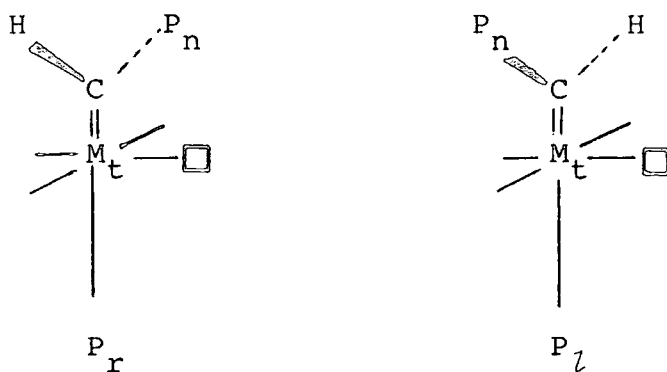
FIGURE 1.15 Tacticity of poly(norbornene)

### 1.9 Stereoregularity and the Olefin Metathesis Reaction

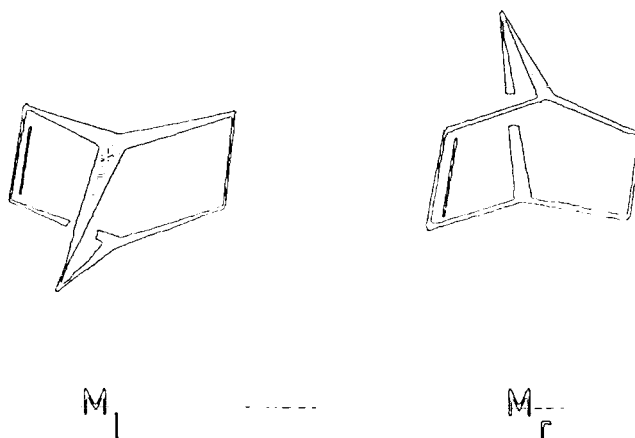
In the olefin metathesis reaction different catalysts give rise to different microstructures. The question as to why this phenomena should occur has been extensively investigated.

#### (a) Formation of *cis* or *trans* double bonds

It is generally accepted that the olefin metathesis reaction proceeds *via* a metallocyclobutane intermediate. One model<sup>67</sup> for the process is based on the proposal that the propagating metallocarbene has octahedral symmetry, one of the positions being a vacant site ( $\square$ ). Two chiral forms are available,  $P_r$  and  $P_l$  (chiral with respect to  $P_n$ , H and  $\square$ , where  $P_n$  represents the growing polymer chain).



In this model the plane containing the metal atom, the carbene carbon and the hydrogen is perpendicular to the vacant site. The reacting norbornene approaches the vacant site of the metallocarbene by its most reactive and least hindered exo face. This it may do in two ways; the bridging methylene (C7) may be orientated into ( $M_r$ ) or out of ( $M_l$ ) the plane of the paper.



Clearly, either of the chiral forms of the metallocarbene may react with either orientation of the olefin. The overall result of one of these possibilities, addition of  $P_L$  and  $M_L$  is shown in Figure 1.16

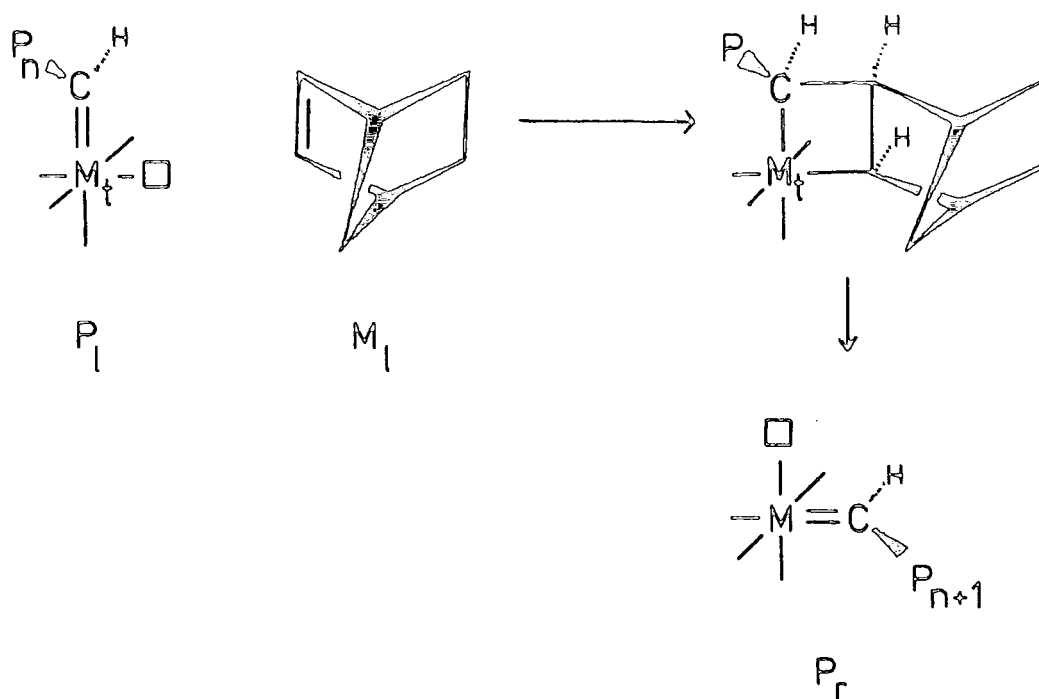


FIGURE 1.16 Addition of  $P_L$  and  $M_L$ .

The reaction leads to the formation of a *cis* double bond, and a metallocarbene at the chain end having the opposite



chirality to the propagating species. Therefore, the mode of addition of monomer,  $M_l$  or  $M_r$ , to the two chiral forms of the metallocarbene,  $P_l$  or  $P_r$ , determines the geometry of the double bond formed and the chirality of the subsequent metallocarbene formed at the chain end. The results of all possibilities are shown in Figure 1.17.

1.  $P_l + M_l \rightarrow P_r$  *cis* double bond
2.  $P_r + M_r \rightarrow P_l$  *cis* double bond
3.  $P_l + M_r \rightarrow P_l$  *trans* double bond
4.  $P_r + M_l \rightarrow P_r$  *trans* double bond.

FIGURE 1.17 Modes and consequences of addition of monomer and metallocarbene

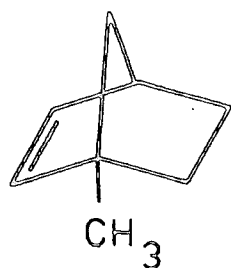
(b) Tacticity effects

The argument outlined above also provides a rationale for the formation of stereoregular polymers. For example, under the constraint that the configurations  $P_l$  or  $P_r$  are preserved between additions, an all *cis* polymer could only result from repetition of steps 1. and 2. This would ultimately lead to the formation of a syndiotactic polymer, since the monomer approaches alternatively in the  $M_l$  and  $M_r$  sense. This results in the incorporation of the cyclopentane rings, in alternately opposed orientations with respect to the polymer backbone. An all *trans* polymer would result from the repetition of steps 3 or 4; this eventually leads to the formation of an all *trans* isotactic polymer since the monomer is repeatedly incorporated into the polymer chain in the same orientation (*i.e.*  $M_l$  or  $M_r$ ). Hence, in this model, *cis* double bonds are associated with a syndiotactic polymer and *trans* double bonds with an isotactic polymer.

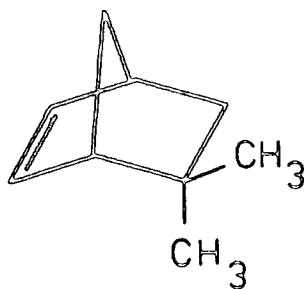
It is thought that an atactic polymer originates from a propagating species that is achiral,  $P_S$ .  $P_S$  may be an octahedral achiral form of  $P_L$  or  $P_R$ , or formed through a chiral species which rapidly epimerizes from the chiral form between successive propagation steps.

(c) Head/Tail Bias in Polymer Chains

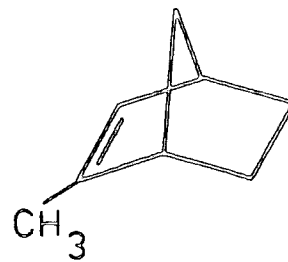
Polymers with a completely regular head/tail structure are observed in some ring opened polymers, especially in cases where the alkene is substituted on or adjacent to the double bond. Thus monomers (19), (20) and (21) all give polymers with a marked degree of HT bias with certain catalysts.



(19)



(20)



(21)

In the particular case of 1-methyl norbornene,<sup>65</sup> polymerization of a racemic mixture using  $\text{ReCl}_5$  as an initiator leads to the formation of an all *cis*, all HT polymer. The formation mechanism of an all *cis* polymer has been described previously (see Section 1.9(a)), *i.e.* by alternation of the two propagation steps shown in Figure 1.17. It is believed that the explanation of the high *cis* specificity of rhenium based catalysts may be a consequence of the fact that the newly formed double bond remains in the coordination sphere

STAGE 1

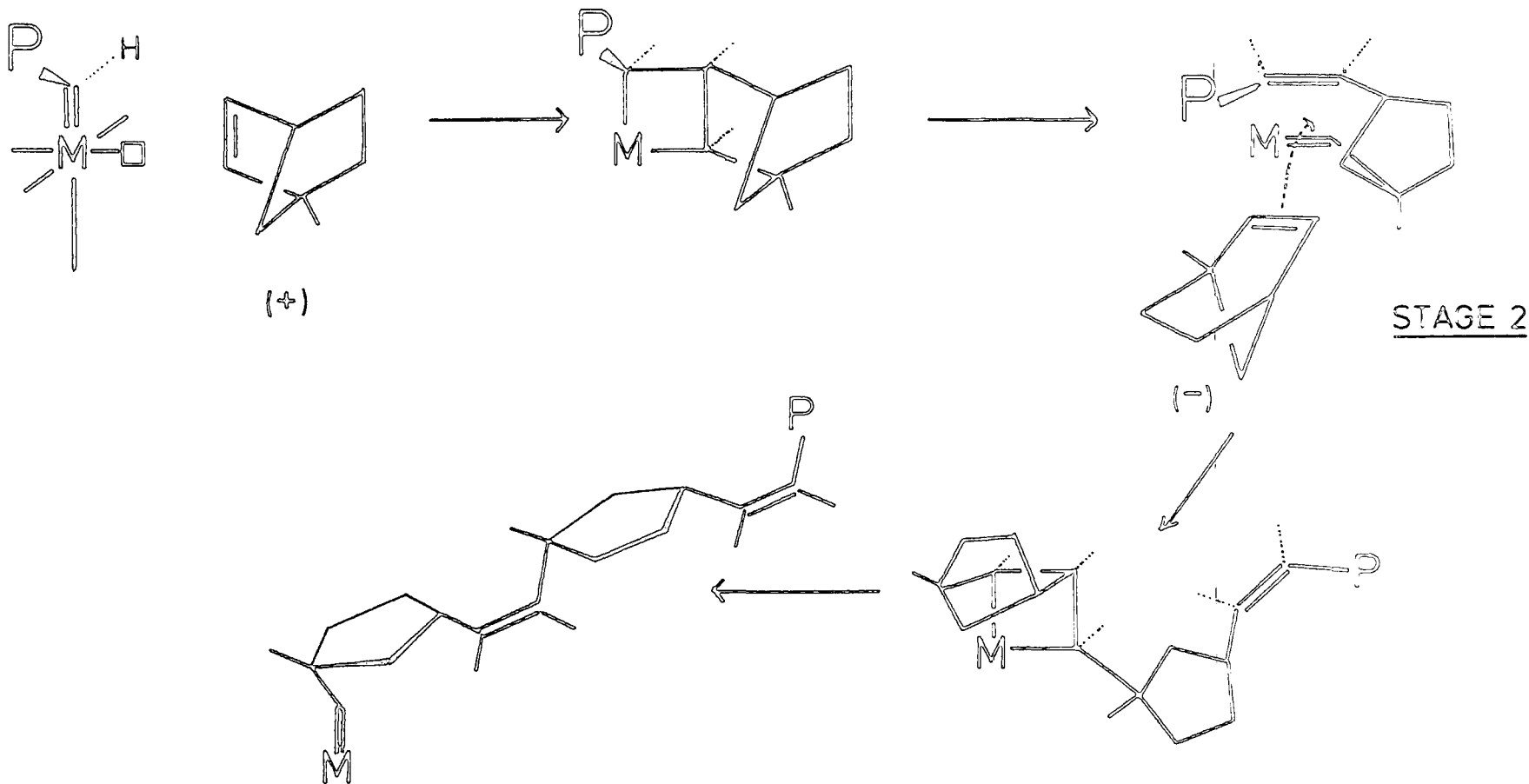


FIGURE 1.18 Stereoregular polymerization of  $\pm$ 1-methylnorbornene to give a *cis* HT syndiotactic polymer

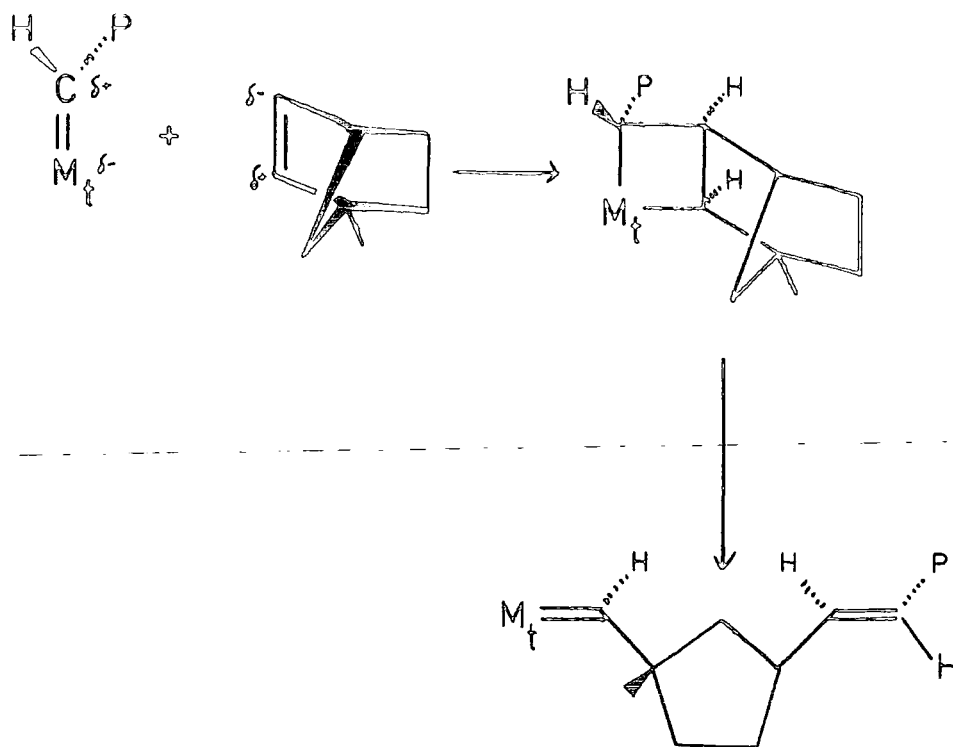
of the metal, the resulting steric constraint favouring the formation of a subsequent *cis* double bond. Figure 1.18 is an attempt to illustrate the consequences of this hypothesis for the case of 1-methyl norbornene polymerization.

Stage 1 is simply the repetition of the process described in Figure 1.16 in which one enantiomer of 1-methyl norbornene has been arbitrarily labelled (+). Stage 2 attempts to show how the incoming monomer approaches the active chain end, displacing the coordinated chain vinylene, and producing a new *cis* double bond. The mode of approach clearly requires that the bridgehead methyl is situated as shown, that is, it must avoid a sterically unfavourable interaction with the catalyst/polymer complex. The inevitable consequence of this steric requirement is that the enantiomers of the monomer are alternatively incorporated in an all HT sense.

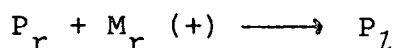
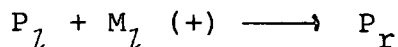
When 1-methyl norbornene was polymerized using  $\text{OsCl}_3$  as initiator the polymer was all *trans* and had a strong HT bias. The metallocyclobutane required to form a *trans* double bond is not so sterically hindered, and in this case the polarity of the metallocarbene and monomer provide a rationale for HT bias. (see diagram over page)

The overall process leads to the repeated formation of HT dyads. The polar and steric dependence of the microstructure of the polymer formed is consistent with a mechanism proceeding *via* a  $2\pi+2\pi$  cycloaddition step, to form a metallocycle (see Figure 1.8).

In the polymerization of optically active 5,5-dimethyl norbornene,<sup>84</sup>  $\text{ReCl}_5$  gives an all *cis*, mostly head to head, tail to tail polymer. Analysis along similar lines to that



described above leads to the conclusion that the only way one enantiomer can be incorporated into the polymer chain is by repetition of the steps



The recurrence of these two processes ultimately leads to a polymer in which the cyclopentane rings have the opposite configurations along the polymer chain (*i.e.* syndiotactic), with HH, TT units. Any HT or TH dyads that are formed are due to the presence of a small amount of (-) enantiomer.

The fact that a HH metallocyclobutane transition state is formed in the 5,5-dimethylnorbornene case is due to the location of the substituents relative to the active centre, creating less steric hindrance. Indeed, attempts to polymerize enantiomerically pure 1-methyl norbornene failed due to the necessity to create a HH metallocyclobutane transition

state, which in this case is sterically forbidden; clearly with no HH units there can only be a maximum of one TT unit in the chain, and consequently no polymer.

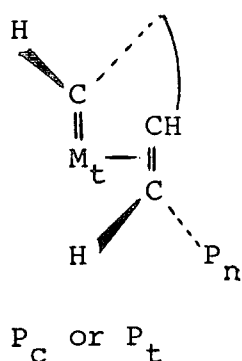
### 1.10 Blockiness in polymer chains

A general trend is observed for polymers of norbornene depending on the fraction of *cis* double bonds,  $\sigma_c$ , present in the chain. Usually for  $\sigma_c < 0.35$  the polymer has a random distribution of *cis* and *trans* double bonds, and for values  $\sigma_c > 0.5$ , a blocky distribution is obtained, that is, *cis* is formed after *cis*, and *trans* after *trans*. It is possible to divide catalysts up into four types depending on the tacticity of the resulting polymer, and these types are listed below.<sup>85</sup>

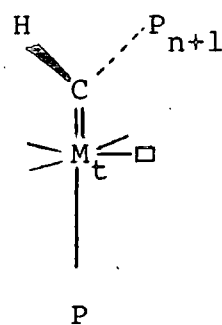
1.  $(\sigma_r)_c \sim (\sigma_m)_t \sim 1.0$  *i.e.* all *cis* vinylenes occur in racemic environments, and all *trans* in meso.
2.  $(\sigma_r)_c \sim (\sigma_m)_t \sim 0.6-0.9$  *i.e.* 60 to 90% of *cis* vinylenes occur in r dyads and 60 to 90% of *trans* are found in m dyads.
3.  $(\sigma_r)_c > (\sigma_m)_t$  *i.e.* a greater proportion of *cis* vinylenes are found in r dyads, than *trans* vinylene in m dyads.
4.  $(\sigma_r)_c \sim (\sigma_m)_t \sim 0.5$  *i.e.* 50% of the *cis* vinylenes are in r dyads and 50% of the *trans* vinylenes are in m dyads.

The first type of behaviour leads to the formation of a polymer in which all the *trans* double bonds are associated with m dyads and all the *cis* double bonds with r dyads. This type of behaviour may be accounted for by postulating that the propagating species  $P_r$  and  $P_l$  (see Section 1.9a) are

kinetically distinct, that is they cannot interconvert between propagation steps. The metallocycle leading to the formation of *cis* double bonds has a dipole resulting in stronger complexation of the newly formed *cis* unit. Consequently, the newly formed *cis* double bond remains within the coordination sphere of the metallocarbene formed at the chain end, and steric factors force the next monomer to add, so as to form another *cis* double bond; this was illustrated in Figure 1.18. When the last formed double bond is *trans*, it is less strongly complexing and moves out of the coordination sphere of the metal; that is,  $P_t$  (the propagating chain end with newly formed *trans* vinylene still in the coordination shell) relaxes immediately to  $P$  (which can be either  $P_l$  or  $P_r$  or Section 1.9a). This sequence of events favours the formation of a subsequent *trans* double bond, since there is least steric hindrance in the metallocycle formed from  $P$ , which is a precursor of a *trans* vinylene. Figure 1.19 illustrates the structures of  $P_c$  or  $P_t$  and  $P$ .



(22)



(23)

FIGURE 1.19 Structures of  $P_c$ ,  $P_t$  and  $P$ .

It is believed that the stability of (22) is dependent on the electron density at the metal site,<sup>86</sup> and anything which

reduces electron density will be stabilising. It is interesting to note that although the metallocarbene need not necessarily have the same oxidation state as the catalyst,  $\text{ReCl}_5$  has a low d orbital occupancy ( $d^2$ ) and gives rise to *cis* double bonds, and  $\text{RuCl}_3$  ( $d^5$ ) has a higher d orbital occupancy and gives rise to polymers with high *trans* contents.

Type 2 behaviour is observed when there is partial racemization of the propagating species to  $P_S$  (*i.e.* the symmetrical metallocarbene of Section 1.9b), and type 4 when there is total racemization,  $P_r \rightleftharpoons P_S \rightleftharpoons P_l$ .

Type 3 behaviour may be explained by assuming that *cis* double bonds remain coordinated to the metal site favouring the production of subsequent *cis* double bonds. *Trans* double bonds are less strongly held and decoordinate. The equilibrium  $P_r \rightleftharpoons P_S \rightleftharpoons P_l$  occurs after formation of *trans* double bonds only and therefore  $(\sigma_m)_t < (\sigma_r)_c$ .

### 1.11 The Reactive face in Norbornene derivatives

In the mechanisms of metathesis postulated above it has been assumed that the exo face of the norbornene monomer is most reactive, which is in agreement with the general reactivity of norbornenes with electrophilic species.<sup>87</sup> This theory receives support from the results of polymerizing a mixture of syn and anti 7-methyl norbornene.<sup>70</sup> When polymerized with a range of catalysts only the anti isomer was incorporated into the polymer. In one case however the syn isomer, recovered from a polymerization in which only the anti isomer was incorporated, was successfully polymerized using



the highly active mesitylene  $W(CO)_3/EtAlCl_2$ /epoxide catalyst. An attempt was then made to polymerize 1,1,7-trimethyl norbornene which was unsuccessful. However, it was found that bicyclo [2.2.2]oct-2-ene, in which the exo and endo faces are equivalent, could be polymerized using this active catalyst system. Thus, although endo attack has been demonstrated to be possible it is clear that unless constraints operate, exo face approach to the catalyst is preferred.

#### 1.12 Application of the Olefin Metathesis Reaction to the Synthesis of Stereoregular Fluoropolymers

The previous sections indicate that stereoregular hydrocarbon polymers are accessible *via* the olefin metathesis reaction. Our approach to the synthesis of stereoregular fluoropolymers was to polymerize a range of fluorinated monomers with a variety of metathesis catalysts, in the expectation that observations made for hydrocarbon systems would be extended to fluorocarbon monomers. Encouragement for this approach came from the results of previous workers;<sup>88-90</sup> fluoropolymers are accessible *via* the olefin metathesis reaction, and different catalysts give rise to polymers with different microstructures.

We believe that stereoregular fluoropolymers may prove to be interesting materials; fluoropolymers in general have attained wide technological importance, and the introduction of stereoregulation into polymer chains often has a profound effect upon polymer properties. Section 1.13 outlines the interesting features of some fluoropolymers, and Section 1.14 indicates the kind of effect stereoregulation can have upon polymer properties.

### 1.13 Range and Uses of Some Common Fluoropolymers

#### (a) Fluorine in Organic Chemistry

Fluorine is unique in its ability to replace hydrogen in a wide range of organic molecules, resulting in a vast change in chemistry and properties.<sup>91</sup> Fluoropolymers represent, in many respects, an extreme in polymer properties. Thus, high thermal and chemical stability are often observed along with other useful properties. However, on the whole, the uses of fluoropolymers are specialised due to the high cost of precursor materials.

#### (b) Some Common Fluoropolymers

##### (i) Poly(tetrafluoroethylene)

Poly(tetrafluoroethylene) is probably the best known of all the fluoropolymers. It is extremely inert to almost any organic compound, a direct result of the kinetic shield provided by the high degree of non-bonded electron density associated with the fluorine atoms. Thus, poly(tetrafluoroethylene) is resistant to attack by solvents up to 300°C, boiling KOH solutions, acids and many other harsh environments. There is a recent report,<sup>92</sup> however, that poly(tetrafluoroethylene), which is a linear polymer, may be dissolved in its oligomers having a chain length of 21 carbon atoms or more, confirming the basic principle that 'like dissolves like'. The uses of the polymer are varied. It is perhaps best known for its use in non stick cookware but also finds applications in protective clothing, wire and cable insulation, pump and valve parts, and generally for the manufacture of components required to operate in aggressive environments.

(ii) Poly(vinylidene fluoride)

Poly(vinylidene fluoride) is a semi crystalline polymer, with good strength properties, and chemical and solvent resistance. The prime use of the polymer, when it became commercially available in 1961, was as a thermoplastic; thus it is used as wire and cable insulating material. One of its more interesting uses however, is as a transducer material, since poly(vinylidene fluoride) displays a greater piezoelectric response than other polymers.<sup>93,94</sup> The polymer has a number of crystalline forms, the piezoelectric response being associated with the  $\beta$  form. The  $\beta$  form may be maximized by elongating the melt produced  $\alpha$  form at elevated temperatures. In the  $\beta$  form the crystallites are arranged in an extended zig-zag, so that the fluorine atoms line up on one side of the polymer chain with the hydrogen atoms on the opposite side, thus producing a dipole. However, overall the crystallites are randomly orientated with respect to each other and poling is required to make the whole film, rather than the individual crystallites, piezoelectric. Poling (that is exposing the film to a high electric field gradient while it is heated above its  $T_g$ ) whilst stretching, creates a material with an unusually large piezoelectric response. The material has found many potential applications and the literature is abundant with patents on the subject. The properties of the polymer which define its uses are its flexibility, light weight and processibility, coupled with its good acoustic match to water and body tissue. Therefore, uses of the piezoelectric material are found in devices to measure breathing rate, heart and pulse rate, in hydrophones, as well as in the audio market in general.

(iii) Poly(vinyl fluoride)

Poly(vinyl fluoride) is commercially available as a highly crystalline, tough flexible film. The polymer shows extreme chemical resistance and thermal stability. It has found large use as a coating and as a glazing material.

(iv) Poly(chlorotrifluoroethylene)

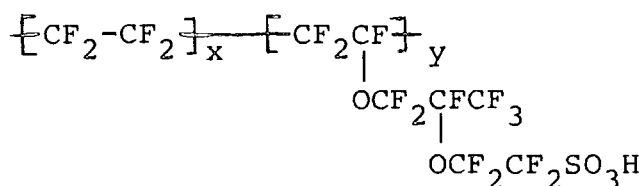
Poly(chlorotrifluoroethylene) is similar to, but inferior to, polytetrafluoroethylene,<sup>95</sup> in many of its properties. Its advantage is that its melt viscosity is low enough for the usual processes of polymer fabrication to be practicable. Typical applications include gaskets, tubing, wire and cable insulation.

(v) Difluoroethylene-hexafluoropropene Copolymer

The copolymer of 1,1-difluoroethylene and hexafluoropropene is renowned for its elastomeric properties. It has found extensive use in many applications where fuel resistant thermally stable elastomers are required, particularly as a fuel line sealant in the aircraft industry.

(vi) Nafion Membranes

Du Pont have developed a series of cation exchange membranes based on a poly(tetrafluoroethylene) backbone with sulphonic acid groups attached at the end of short side chains based on the perfluoropropylene ether unit.



Membranes formed from this polymer are called Nafion,<sup>95</sup> and are used in the electrochemical production of chlorine and caustic soda.<sup>97</sup> Traditionally these materials were produced employing a mercury or diaphragm cell, the Nafion membrane replaces the diaphragm in such systems.

Nafion has also found use as a catalyst for a wide variety of organic reactions.<sup>98,99</sup>

### (c) Conclusions

Fluoropolymers clearly have interesting and varied properties and make a significant contribution to current technologies. The synthesis of new fluoropolymers, therefore seems a worthwhile topic of research.

#### 1.14 Stereoregulation in Polymer Chains and property dependence

The recognition, study and exploitation of the stereoregular polymerization of alkenes is one of the more notable recent achievements of polymer science.<sup>100</sup> An ability to regulate the fine details of microstructure extends the range of materials accessible from a particular monomer, and frequently there are spectacular differences in the properties of a stereoregular product and its atactic analogue.

Stereoregular polymerization of alkenes is usually associated with the use of Ziegler Natta catalysts (although as described earlier, the olefin metathesis reaction gives stereoregular products, and it is postulated that the two processes are closely related<sup>101</sup>). Ziegler<sup>102</sup> discovered in 1952, that ethylene could be polymerized at low pressure in

the presence of a mixture of transition metal compound and aluminium alkyl. Shortly afterwards Natta<sup>103</sup> applied the Ziegler catalyst to propene, and showed that the polymerization could be regulated to give isotactic, syndiotactic and atactic forms of the polymer. The different forms of polypropene display well the property differences that may occur; thus atactic polypropene is a mechanically weak waxy material which is virtually useless, whereas the isotactic form is a tough thermoplastic and has a range of uses. The isotactic form has high heat resistance and tensile strength, good optical clarity and low specific density. Its applications include injection moulded items from food containers to car bumpers, and as a film it is used extensively for packaging applications.

Polymers of the higher olefins can be produced using Ziegler-Natta catalysts. Typically isotactic polyolefins exhibit higher mechanical strength and chemical stability than their atactic equivalents.

### 1.15 Stereoregular Fluoropolymers

#### (a) General

In view of the general outline of the properties associated with fluoropolymers, and the obvious beneficial effect stereoregulation can have upon polymer properties, it is perhaps surprising that the literature contains very few references to stereoregular fluoropolymers. As far as we are aware there are none available commercially.

(b) Specific Work on Stereoregular Fluoropolymers

Some work has been carried out on the polymerization of some fluorinated alkenes using Ziegler-Natta catalyst systems. In 1962, Overberger<sup>104</sup> set out to determine if a catalyst system could be found for the Ziegler-Natta polymerization of some fluorinated monomers. A vanadium trichloride, tri-isobutyl aluminium catalyst was found to be effective for the polymerization of 4,4,4-trifluorobut-1-ene, 5,5,5-trifluoromethylpent-1-ene, 3-trifluoromethylbut-1-ene and 4-trifluoromethylpent-1-ene. 3,3,3-Trifluoroprop-1-ene could not be polymerized; it was concluded that the polar perfluoroalkyl groups must be at least one carbon atom removed from the double bond before polymerization can occur. In all cases, substitution of a  $\text{CH}_3$  for a  $\text{CF}_3$  caused an increase in melting point,<sup>105</sup> and all polymers prepared using the  $\text{VCl}_3$  based catalyst had higher melting points than their radically derived analogues, which is consistent with some measure of stereoregulation. A later publication by the same author<sup>106</sup> was concerned with reactivity rather than an investigation into microstructure.

Haszeldine<sup>107</sup> published some work on the Ziegler-Natta polymerization of vinyl fluoride. The best catalyst system was prepared from vanadium oxychloride, tri-isobutyl aluminium and tetrahydrofuran. The kinetics of the reaction were followed and were found to show typical Ziegler-Natta parameters. However, no discussion of any examination of microstructure of the polymer chains was presented.

There has been a comparatively large amount of work published on the microstructure of polymers of the simple fluorinated alkenes and their copolymers.<sup>108-114</sup> Thus Tonelli<sup>108,109</sup>

has compared the actual and calculated microstructures of poly(trifluoroethylene), poly(vinylidene fluoride) and poly(vinyl fluoride). The microstructure of the polymers may be predicted from bond rotation probabilities obtained from conformational models.<sup>115-120</sup> In all cases, the predicted and actual microstructures obtained compared favourably. All polymers showed a mostly head/tail structure, with a minor amount of head to head, tail to tail mode of addition,<sup>121,122</sup> and all polymers were atactic.

Cais<sup>112</sup> has looked at the microstructure of six fluoroethylenes. He prepared all head to tail poly(trifluoroethylene) by dechlorination or debromination of the precursor polymers, poly(bromotrifluoroethylene) or poly(chlorotrifluoroethylene). The polymers were not, however, stereoregular. Lee<sup>123</sup> *et al* have investigated the microstructure of some fluorinated methacrylate polymers. The microstructures of the polymers were determined by <sup>1</sup>H nmr spectroscopy. Commercially available fluorinated methacrylate monomers had bulky side groups containing protons. Overlap of the side chain and backbone resonances made interpretation of spectra, and hence microstructure determination, difficult. To avoid this the authors prepared some special methacrylate monomers. 1,1-Dihydroheptafluorobutyl methacrylate and pentafluorophenyl methacrylate were prepared and polymerized *via* emulsion techniques at 5°C. The polymers produced were reported to be predominately syndiotactic. Similarly Pittman<sup>124</sup> assigned the microstructure of poly(methyl  $\alpha$ -fluoroacrylate) as syndiotactic.

### (c) Conclusions

The summary above illustrates that little work has been



carried out on the synthesis of stereoregular fluoropolymers.

#### 1.16 Objectives of the Work described in this thesis

Our objectives were to synthesise some new stereoregular fluoropolymers. Our approach was to prepare some fluorinated norbornene derivatives and polymerize them with a range of available metathesis catalysts. The microstructures of the polymers thus produced were investigated using  $^{13}\text{C}$  nuclear magnetic resonance and infrared spectroscopy. The properties of the polymers were investigated and an attempt to correlate property and microstructure was undertaken. Hence, the monomers shown in Figure 1.20 have been prepared and investigated during the course of this work.

Chapter Two describes the synthesis and characterization of these monomers. Chapter Three is concerned with the metathesis ring opening polymerization and microstructure determination of monomers (I)-(IV). In Chapter Four the polymerization of monomers (V)-(X) is discussed, as a survey of the type of monomer which will undergo metathesis. Chapter Five attempts to correlate the microstructure obtained with the physical properties observed.

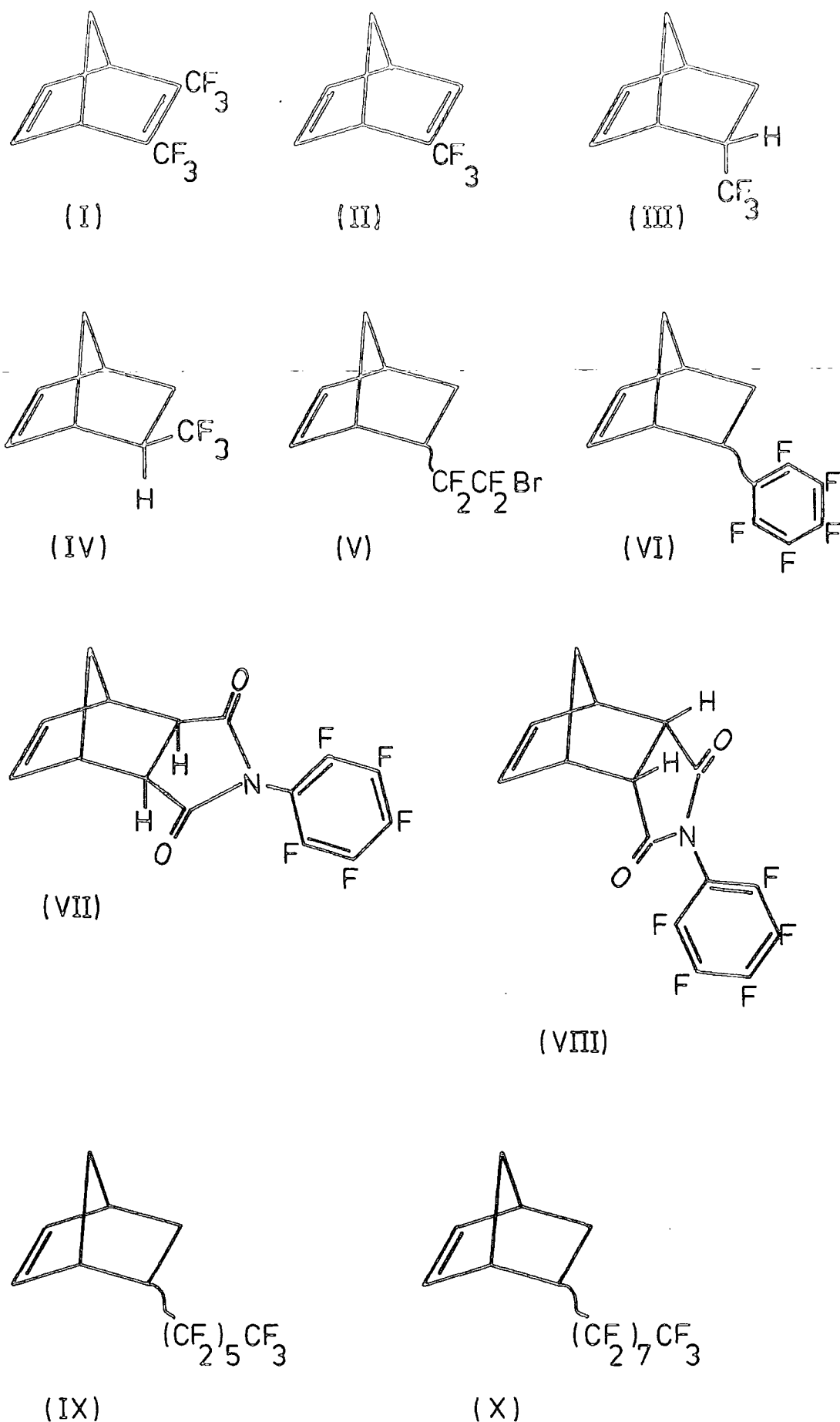


FIGURE 1.20 Compounds synthesised as potential monomers for metathesis ring opening polymerization

CHAPTER TWO

SYNTHESIS AND CHARACTERIZATION OF MONOMERS

## 2.1 The Diels Alder Reaction

The monomers synthesised during the course of this work have been made either directly *via* a Diels Alder reaction, or by further reaction of a Diels Alder adduct to yield the desired product.

In the Diels Alder reaction a compound containing a double or triple bond, the dienophile, adds to a conjugated diene to form a product containing a six-membered ring, as shown in Figure 2.1.



FIGURE 2.1 The Diels Alder reaction between a dienophile and conjugated diene

In the reaction two new  $\sigma$  bonds are formed at the expense of two  $\pi$  bonds in the starting materials. The reaction is favoured by the presence of electron withdrawing groups on the dienophile and electron donating substituents on the diene, or alternatively, electron withdrawing groups on the diene and electron donating substituents on the dienophile. The diene must be in the *cis* configuration before it will react; reaction of a *trans* diene would result in a product with a high degree of strain and this type of reaction is not observed. Cyclopentadiene in which the double bonds are held in the *cis* configuration is highly active in Diels Alder reactions, and has been used exclusively as the diene

during the course of this work.<sup>125</sup> The reaction of cyclopentadiene with a fluorinated dienophile would be expected to occur fairly readily; this is indeed the case, and the product is a strained bicyclic compound in which the fluorine substituents are remote from the double bond.<sup>126,127</sup> An unsymmetrical dienophile may add to cyclopentadiene in two possible ways, giving rise to *exo* and *endo* isomers. This is illustrated in Figure 2.2, where  $R_f$  represents a perfluoroalkyl group.

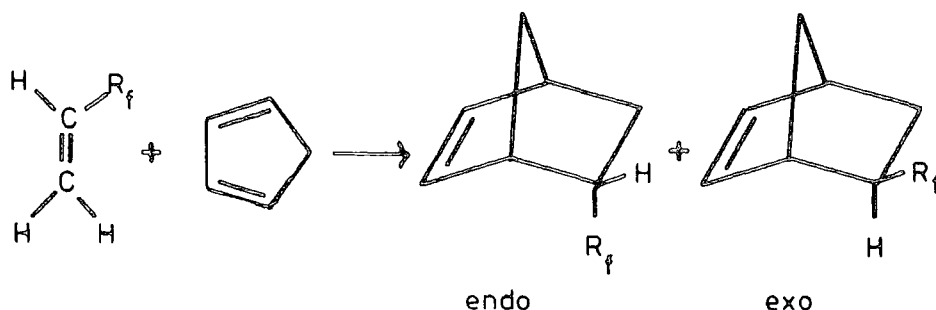


FIGURE 2.2 Diels Alder reaction between an unsymmetrical dienophile and cyclopentadiene

The ratio of *exo* and *endo* adducts formed in a reaction is dependent upon the experimental conditions; the *exo* adduct is generally favoured at equilibrium, and the *endo* adduct usually predominates under conditions of kinetic control.

The reaction is highly stereospecific, and the geometry of the dienophile is maintained in the adduct.

## 2.2 Synthesis and Characterization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene(I)

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene(I) has been used extensively in these laboratories as a potential monomer for the olefin metathesis reaction.<sup>88</sup> It was synthesised *via* the Diels Alder reaction between hexafluorobut-2-yne and cyclopentadiene as shown in Figure 2.3.

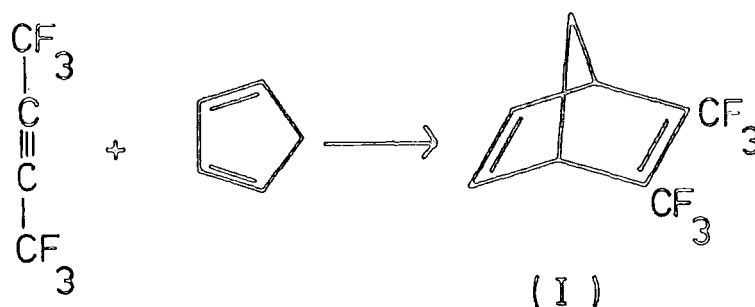


FIGURE 2.3 Diels Alder reaction between cyclopentadiene and hexafluorobut-2-yne

The infra-red spectrum of the product (Appendix B, 1) was identified with that of an authentic sample. The monomer was stored over maleic anhydride to remove any trace amounts of cyclopentadiene, and vacuum transferred from the solid residues when required. Although this monomer has been characterized previously, during the course of this work better quality high field nmr spectra were obtained and spectra data are tabulated in Tables 2.1 and 2.2.

TABLE 2.1  $^1\text{H}$  nmr shifts and assignment of monomer I,  
recorded at 300.13 MHz, TMS internal standard

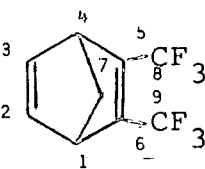
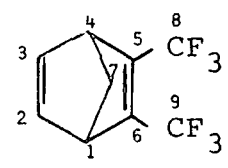
Compound	Shift/ ppm.	Multiplicity	Inte- gral	Assign- ment
	6.92	resolved into three lines separated by 1.95 Hz	1	2, 3
	3.90	broad unresolved signal FWHM $\sim 5\text{Hz}$	1	1, 4
	2.17	ABq, $\delta_A=2.08$ , $\delta_B=2.26$ , $J_{AB}=6.95\text{Hz}$ B limbs resolved into three lines separated by 1.63Hz. A limb unres- olved, FWHM $\sim 5\text{Hz}$	1	7

TABLE 2.2  $^{13}\text{C}$  Nmr shifts and assignments of Monomer I,  
recorded at 75.45 MHz, TMS internal reference

Compound	Shift/ ppm	Multiplicity	Assignment
	149.4	s	2, 3
	142.9	s	5, 6
	122.9	q, $^1J_{\text{C-F}}=270\text{Hz}$	8, 9
	74.0	s	1, 4
	53.3	s	7

### 2.3 Synthesis and Characterization of 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene(II)

2-Trifluoromethylbicyclo[2.2.1]hepta-2,5-diene was synthesised *via* the Diels Alder reaction between 3,3,3-trifluoropropyne and cyclopentadiene.<sup>88</sup> 3,3,3-Trifluoropropyne is available commercially, but at high cost, which made its synthesis by the established route<sup>128</sup> preferable. The reaction of 3,3,3-trifluoro-1,1,2-trichloropropene with a mixture of zinc metal and zinc chloride in N,N-dimethyl acetamide gave 3,3,3-trifluoropropyne in 68% yield. The infra-red spectrum (Appendix B,2) was in agreement with that recorded previously. Figure 2.4 outlines the synthetic procedure to obtain monomer(II).

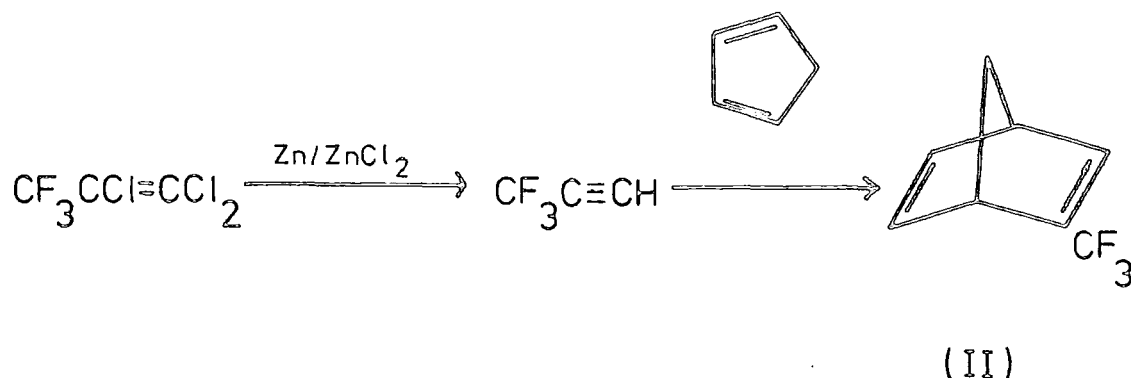


FIGURE 2.4 Synthesis of 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene(II)

The synthesis of 3,3,3-trifluoropropyne, 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene and some of its subsequent polymerizations, were carried out in collaboration with Mr. P.C. Taylor, a third year honours degree project student. All the data are discussed, and the students' contributions are specifically identified. 2-Trifluoromethyl bicyclo-



[2.2.1]hepta-2,5-diene was characterized by infra-red spectroscopy (Appendix B,3), mass spectrometry (Appendix C,1), elemental analysis and n.m.r. spectroscopy. All data were in agreement with that reported previously.<sup>88</sup>

#### 2.4 Synthesis and Characterization of Exo and Endo 5-trifluoromethyl bicyclo[2.2.1]hept-2-ene (III and IV)

The Diels Alder reaction between cyclopentadiene and 3,3,3-trifluoropropene gave a mixture of exo and endo isomers of 5-trifluoromethyl bicyclo[2.2.1]hept-2-ene as the major products, together with small amounts of diene dimer and poly-adducts (Figure 2.5).

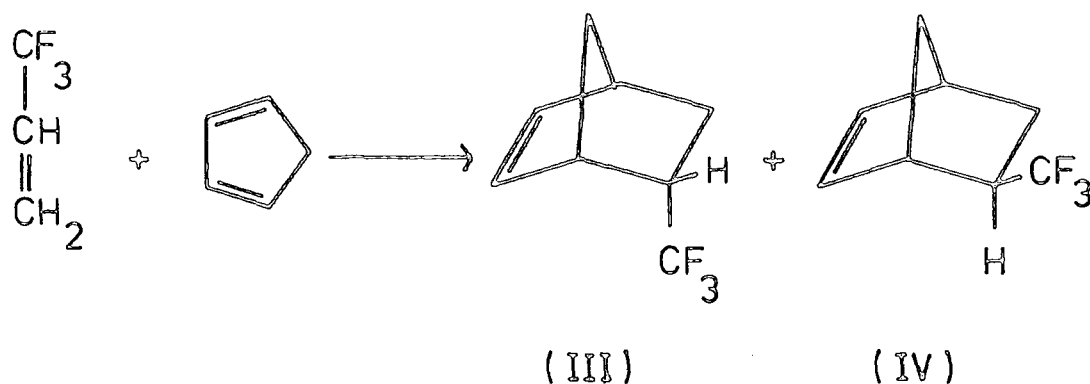


FIGURE 2.5 Diels Alder reaction between 3,3,3-trifluoropropene and cyclopentadiene

The 1:1 adducts were recovered by distillation. The ratio of exo and endo isomers formed in the mixture can be conveniently determined using <sup>19</sup>F n.m.r. spectroscopy, the exo and endo adducts giving resonances at quite distinct chemical shifts. Earlier reports in the literature indicated some dispute over the assignment of the signals. In the past workers have used the generalisations of Smart and Stone,<sup>129,130</sup>

who asserted that fluorine atoms or trifluoromethyl groups in exo positions in norbornene derivatives occur at lower field than those in endo positions. However, a relatively recent report<sup>131</sup> which deals specifically and in some detail with the stereochemistry of the reaction between cyclopentadiene and 3,3,3-trifluoropropene assigns the lower field signal in the  $^{19}\text{F}$  n.m.r. to the endo adduct. This reassignment is based on a detailed analyses of the high field  $^1\text{H}$  n.m.r. spectra of both adducts and is much better founded than the earlier shift correlations. The newer assignment is also consistent with the results obtained by varying the reaction conditions (see below) and we conclude that the signal at 68.0 ppm (doublet  $^3J_{\text{H-F}}=15\text{Hz}$ ) is associated with the exo adduct, and at 66.1 ppm (doublet  $^3J_{\text{H-F}}=15\text{Hz}$ ) with the endo adduct.

The reaction was carried out under different conditions and the variation in the  $^{19}\text{F}$  n.m.r. integrations monitored, as shown in Table 2.3.

Temperature	Reaction time/days	$^{19}\text{F}$ Nmr Integration		Yield %
		68.0 ppm	66.1 ppm	
20	3	10.6	100	3
160	3	37.0	100	72
200	7	55.5	100	75

TABLE 2.3 Variation of the Relative Values of the  $^{19}\text{F}$  n.m.r. integrations for monomers III and IV as a function of reaction conditions

Generally in Diels Alder reactions the endo adduct is produced under conditions of kinetic control whereas the exo isomer is formed at equilibrium.<sup>132</sup> The results illustrated in Table 2.3

are therefore consistent with the assignment of the isomer displaying a  $^{19}\text{F}$  resonance at 68.0 ppm to the exo form, and the signal at 66.1 ppm to the endo form.

Separation of the isomers by distillation was attempted using the best equipment available, Fischer Spaltrahr system 0200/01 concentric tube column, 90 plates, and very low hold up. Although enrichment of isomers was achieved total separation could not be accomplished. However, it was found that the isomers could be separated by preparative scale gas chromatography (10% DNP on Celite at  $100^{\circ}\text{C}$ ). This method of separation was slow and only small amounts of monomer were obtained by this procedure.

The infra-red spectra of the adducts (Appendix B, 4 and 5) were consistent with the required products; both showed the expected vinylic C-H ( $3060\text{ cm}^{-1}$ ),  $-\text{CH}=\text{CH}-$  ( $1620\text{ cm}^{-1}$ ) and C-F ( $1000-1300\text{ cm}^{-1}$ ) absorptions. The mass spectra of the adducts showed molecular peaks at 162, and base peaks at 66 ( $\text{C}_5\text{H}_6^+$ ) resulting from a retro Diels Alder reaction. The  $^1\text{H}$  n.m.r. of an exo/endo mixture was complicated, but similar to that reported previously.<sup>88,131</sup>

## 2.5 Attempted Alternative Synthesis of Endo 5-trifluoromethyl bicyclo[2.2.1]hept-2-ene

Preparative gas chromatography is unsuitable for separating a large amount of monomer, hence an alternative method for the synthesis of either exo or endo 5-trifluoromethylnorbornene was sought. A potential route for the synthesis of the endo isomer is illustrated in Figure 2.6.

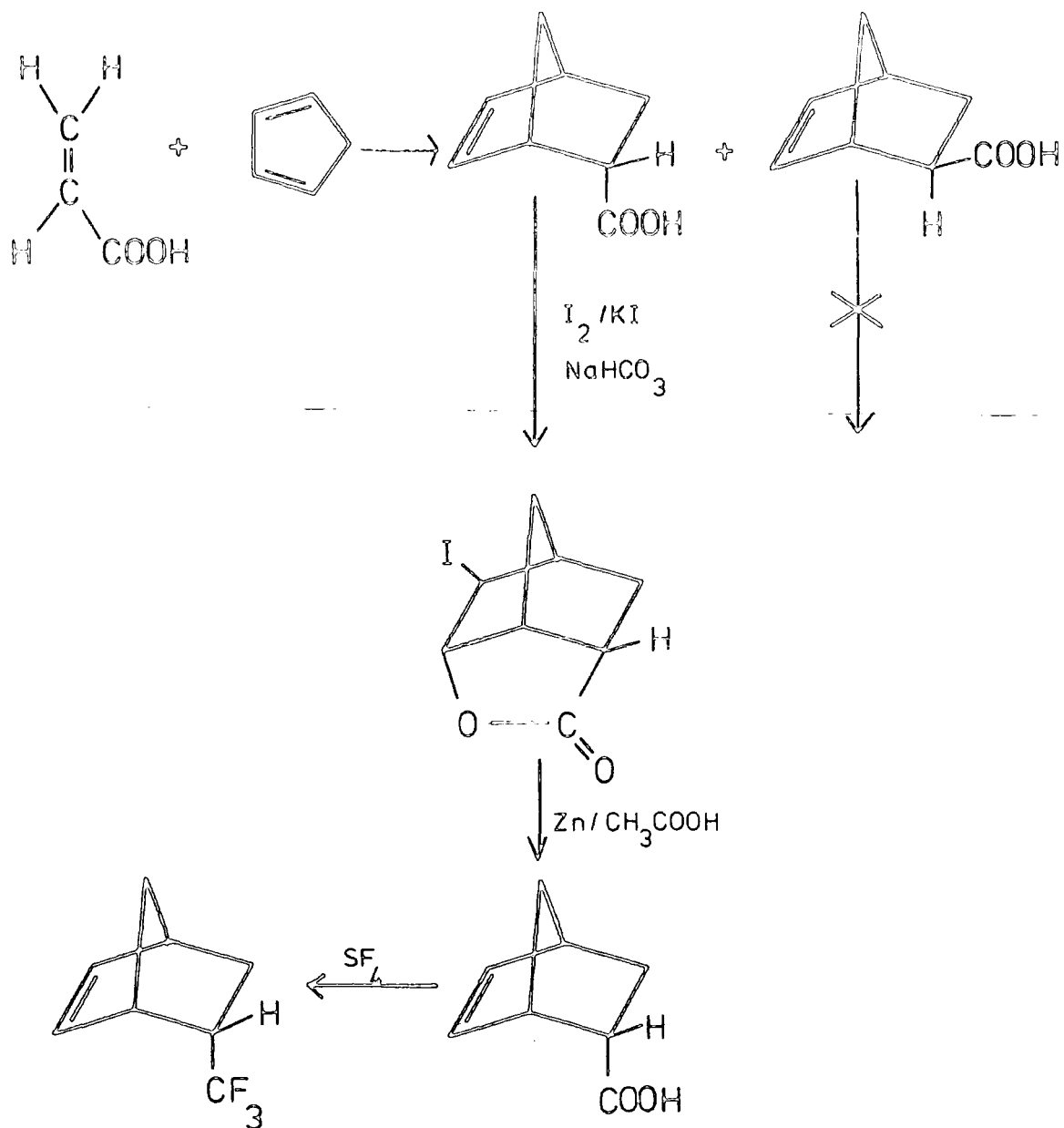


FIGURE 2.6 Potential route for the synthesis of pure endo 5-trifluoromethyl bicyclo[2.2.1]hept-2-ene

This route, if successful would satisfy a number of requirements; it would:

- (i) provide an unambiguous proof of endo stereochemistry;
- (ii) avoid gas chromatographic separation and allow easy scale up;
- (iii) provide a route to pure enantiomers since endo-5-carboxylic acid bicyclo[2.2.1]hept-2-ene can be resolved.

The Diels Alder reaction between cyclopentadiene and acrylic acid is well established and was easily accomplished, following the literature method.<sup>133</sup> The next stage in the sequence provides a means of separating exo and endo isomers; as a result of the geometry of the carboxylic acid with respect to the double bond, the endo acid readily forms an iodolactone, whereas the exo acid does not.<sup>134</sup> The iodolactone is a crystalline material (infra-red spectra, Appendix B,6) which was easily separated from any exo acid that was present in the mixture. The first two stages were performed successfully.

However, the regeneration of the free acid from the iodolactone was performed several times without any appreciable yield.<sup>134</sup> Before refining this reaction to increase the yield of endo acid, the reaction of sulphur tetrafluoride with the easily obtained exo/endo mixture of the free acid was undertaken, in an attempt to assess the feasibility of the experimental procedure. Fluorination of the acid mixture was attempted under relatively mild conditions for the reagent<sup>135</sup> (autoclave, 80°C, 28 atm). However, only black intractable tars were obtained from which no organofluorine compounds could be isolated. It is significant in this context that previous workers have experienced some unusual results when using this reagent, and it seems it does not have the wide applicability that is generally supposed. The synthesis of 4,4-difluorocyclopentene, shown in Figure 2.7 was attempted by Wilson<sup>88</sup> but a low yield of the material provisionally assigned as compound (24) was obtained, although fluorination of cyclopentanone gave the expected 1,1-difluorocyclopentane in ~70% yield.

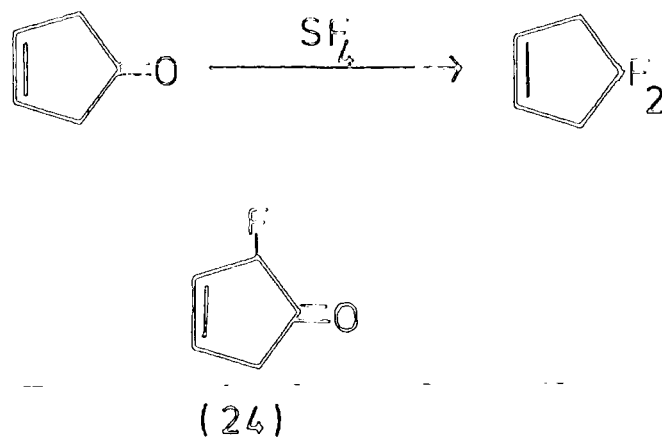


FIGURE 2.7 Anticipated and actual result of the reaction of cyclopentene-4-one with sulphur tetrafluoride

In view of the above difficulties this approach was discontinued.

2.6 Synthesis and characterization of 5-(2-bromotetrafluoroethyl bicyclo[2.2.1]hept-2-ene (V)

5-(2-Bromotetrafluoroethyl)bicyclo[2.2.1]hept-2-ene was synthesized *via* the Diels Alder reaction between cyclopentadiene and 3,3,4,4-tetrafluoro-4-bromobut-1-ene, as illustrated in Figure 2.8

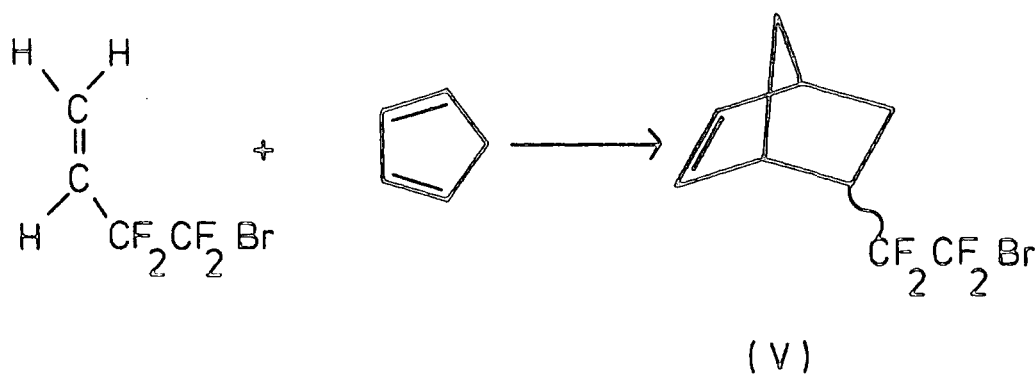


FIGURE 2.8 Diels Alder reaction between cyclopentadiene and 3,3,4,4-tetrafluoro-4-bromobut-1-ene (V)

The product consisted of both exo and endo isomers which could not be separated by distillation or chromatographic techniques, and the monomer was characterized as a mixture. The mass spectrum (Appendix C,4) showed the expected bromine isotope pattern with signals of equal intensity at 272 and 274 mass units (parent ion) and at 129 and 131 ( $\text{CF}_2\text{Br}^+$ ). The base peak was observed at 66 mass units, resulting from a retro Diels Alder reaction ( $\text{C}_5\text{H}_6^+$ ). The infra-red spectrum was complex (Appendix B,7) but showed the expected vinylic CH ( $3025\text{ cm}^{-1}$ ),  $-\text{CH}=\text{CH}$  ( $1620\text{ cm}^{-1}$ ), C-F ( $1050\text{--}1150\text{ cm}^{-1}$ ) and C-Br ( $710\text{ cm}^{-1}$ ) absorptions.

In the past the interpretation of the  $^{19}\text{F}$  n.m.r. spectra of fluorinated bicyclo[2.2.1]hept-2-enes has been based on the correlations asserted by Smart and Stone, as discussed previously. However, in the case of 5-trifluoromethyl bicyclo[2.2.1]hept-2-ene these assignments have now been reversed and this raises the question of whether the generalisations are applicable to other 5-substituted fluorinated norbornene systems. Several reports by McBee<sup>136-139</sup> state that fluorine substituents dominate the stereochemical course of the Diels Alder reaction. He has extensively investigated the stereochemistry of the Diels Alder reactions depicted in Figure 2.9 as a function of the substituent X.

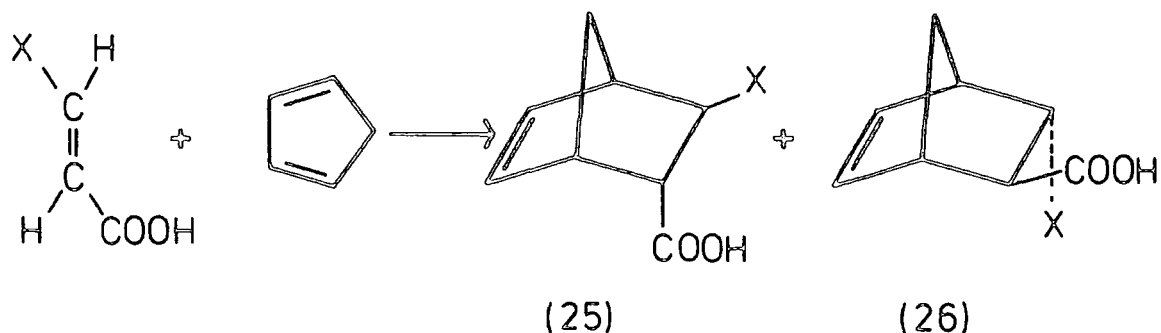


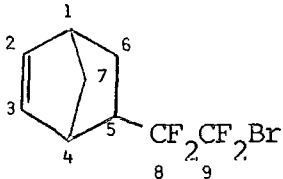
FIGURE 2.9 Diels Alder reaction between Cyclopentadiene and a substituted acrylic acid

When X was a hydrogen atom the endo H content was 37.4% (*i.e.* the product mixture consisted of 37.4% of (26) and 62.6% of (25)). When the hydrogen is replaced by a trifluoromethyl group the product mixture was now found to contain 73% endo  $\text{CF}_3$  groups and due to the stereospecific nature of the Diels Alder reaction the carboxyl group is forced into the exo position. It is apparent that the trifluoromethyl group is endo directing, and this provides further support for the assignment of signals in the  $^{19}\text{F}$  n.m.r. spectrum of 5-trifluoromethyl norbornene discussed earlier. When X was a larger perfluoroalkyl group the endo content remained high; and there was no evidence that large perfluoroalkyl groups were forced into the less sterically hindered exo position.

In view of these results it seems that a  $\text{CF}_3$  and a  $\text{CF}_2\text{CF}_2\text{Br}$  substituent would have similar stereochemical consequences in the Diels Alder reaction. Hence the reaction between cyclopentadiene and 3,3,4,4-tetrafluoro-4-bromobut-1-ene would be expected to yield a high proportion of endo adduct, and if this is assumed the  $^{19}\text{F}$  n.m.r. spectrum can now be assigned by associating the high intensity peaks with the endo isomer. The shifts and assignments are given in Table 2.4.



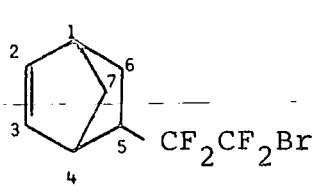
TABLE 2.4  $^{19}\text{F}$  N.m.r. Shifts and Assignments of endo/exo 5-(2-bromotetrafluoroethyl)bicyclo[2.2.1]hept-2-ene recorded at 56.45 MHz.

Compound	Shift/ ppm.	Multiplicity	Integral	Assignment
	111.7	ABq, $\delta_{\text{A}}=109.6$ , $\delta_{\text{B}}=113.8$ , $J_{\text{AB}}=272.8\text{Hz}$ . Each limb split into doublet $^3J_{\text{H-F}}=18.8\text{Hz}$ .	3	8,endo
	109.9	Abq, $\delta_{\text{A}}=107.7$ , $\delta_{\text{B}}=112.1$ , $J_{\text{AB}}=263.4\text{Hz}$ . Each limb split into doublet $^3J_{\text{H-F}}=18.8\text{Hz}$	1	8,exo
	64.5	s	3	9,endo
	63.5	s	1	9,exo

The endo adduct displays a resonance at lower field than the exo isomer and this is consistent with the assignment of signals in the  $^{19}\text{F}$  n.m.r. of 5-trifluoromethyl bicyclo[2.2.1]-hept-2-ene. The ratio of endo to exo adducts in the mixture was 3:1 as calculated from the integral of the appropriate signals.

The  $^1\text{H}$  n.m.r. of the mixture of adducts was complicated and has not been interpreted in detail. Nevertheless the ratio of the integrals of the vinyl, methine and methylene signals was consistent with the above assignment. The shifts and assignments are given in Table 2.5.

TABLE 2.5  $^1\text{H}$  N.m.r. Shifts and Assignments of 5-(2-bromotetrafluoroethyl) bicyclo[2.2.1]hept-2-ene recorded at 250 MHz.

Compound	Shift	Multiplicity	Integral	Assignment
	6.1	broad s)	2	2,3
	5.9	" )		
	3.1	broad m)	3	1,4,5
	2.8	" )		
	1.7	" )	4	6,7
	1.3	" )		

### 2.7 Synthesis and Characterization of 5-pentafluorophenyl bicyclo[2.2.1]hept-2-ene (VI)

Cyclopentadiene and 1,2,3,4,5-pentafluorostyrene react to give 5-pentafluorophenylbicyclo[2.2.1]hept-2-ene as a mixture of exo and endo isomers (Figure 2.10).

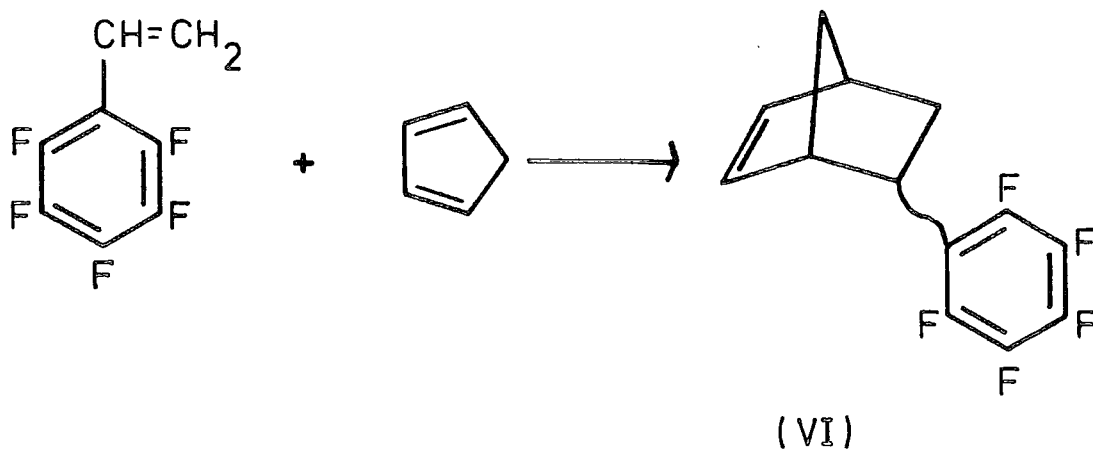
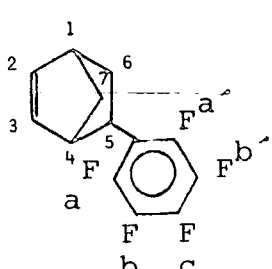


FIGURE 2.10 Diels Alder reaction between pentafluorostyrene and cyclopentadiene

The fluorines of the pentafluorophenyl group are electron withdrawing through the  $\sigma$  framework and overall the pentafluorophenyl group is probably electron withdrawing. Hence, the reaction illustrated in Figure 2.10 might be expected to be a conventional Diels Alder reaction and to give a product with a high endo pentafluorophenyl group content. On consideration of the geometry of the molecule with the aid of molecular models, it appears that on steric grounds the pentafluorophenyl group would be preferentially located in the exo position. In the transition state leading to the endo adduct it seems that, due to the large steric bulk of the pentafluorophenyl group, an unfavourable interaction occurs between the  $\pi$  electrons of the double bond and the ortho fluorines of the pentafluorophenyl unit. On the other hand, in the transition state leading to the exo adduct, there is the chance of a favourable electrostatic interaction between the ortho fluorines and bridgehead hydrogens. This would favour formation of the exo adduct. Thus, these considerations suggest that for the fluoroaryl substituted dienophile steric and electronic factors may favour the exo isomer more than in the perfluoroalkyl substituted case. On inspection of the  $^{19}\text{F}$  n.m.r. of the product it was found that the ortho fluorine signals are resolved for the exo and endo isomers, and the highest intensity signal corresponded to the resonance at lowest field, *i.e.* the signal we would expect to be associated with the exo adduct in perfluoroalkyl substituted norbornenes. However, in the endo adduct the ortho fluorines are situated in close proximity to the olefinic unit and might reasonably be expected to experience a downfield shift; thus it is impossible to make an unambiguous assignment on the basis of the  $^{19}\text{F}$  n.m.r. data recorded in Table 2.6.

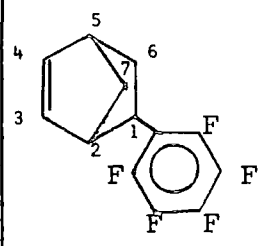
TABLE 2.6 <sup>19</sup>F N.m.r. signals and assignments recorded at 56.45MHz, CCl<sub>3</sub> external reference

Compound	Shift/ ppm	Multiplicity	Integral	Assignment
	164.9	d. of d. of d. $J_{ab}=22.6\text{Hz}$ , $J_{bc}=20.7\text{Hz}$ , $J_{a'b'}=6.3\text{Hz}$	2	b(+b')
	160.2	t, $J_{bc}=20.7\text{Hz}$	1	c
	142.5	d. of d, $J_{ab}=22.9\text{Hz}$ $J_{ab'}=5.6\text{Hz}$	0.65	exo a+a'
	140.8	d. of d, $J_{ab}=22.9\text{Hz}$ $J_{ab'}=5.6\text{Hz}$	1.3	endo a+a'

The <sup>1</sup>H n.m.r. spectrum run at 250 MHz provided evidence for the assignment of the major isomer as endo. Although the spectrum was complicated the signals in the vinylic region were assigned on the basis that a 2:1 ratio of endo:exo adducts was formed. In the vinylic region multiplets at 6.25 and 6.15 (2:1 ratio respectively), and 5.96 and 5.92 ppm (1:2 ratio respectively) were observed. The highest and lowest field signals in this region were assigned to the endo adduct and the two central signals to the exo adduct. On consideration of the geometry of the molecule, in the exo adduct the fluorine substituents are far removed from the double bond and are expected to have relatively little effect on the position at which these signals appear. In the endo adduct, by contrast, there is a potentially strong interaction between the ortho fluorines of the pentafluorophenyl group and one of the protons at the double bond, causing a large difference in shift between the two vinyl positions. Although

these assignments are self consistent and in reasonable agreement with the expected result they do not constitute a rigorous proof. A higher field spectrum may provide sufficient resolution to allow a more detailed analysis and provide confirmation of our assignment. The shifts and assignments of the  $^1\text{H}$  n.m.r. are given in Table 2.7.

TABLE 2.7  $^1\text{H}$  N.m.r. shifts and assignments of 5-pentafluorophenyl bicyclo[2.2.1]hept-2-ene, TMS external reference

Compound	Shift	Multi- plicity	Integral	Assign- ment
	6.25	m	2	4 endo
	6.15	m	1	4 exo
	5.96	m	1	3 exo
	5.92	m	2	3 endo
	3.50	m	)	)
	3.22	s	)	)
	3.11	s	) 9	) 1,2,5
	3.00	s	)	)
	2.19	m	)	)
	1.65	m	) 12	) 6,7

Hence, although the data confirms the structure of the product the ratio of exo and endo isomers can only be provisionally assigned.

The infrared spectrum (Appendix B,8) and mass spectrum (Appendix C,5) were consistent with the structure assigned.

2.8 (a) Synthesis and Characterization of *exo*-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (VII)

*Exo*-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide was prepared by the route depicted in Figure 2.11

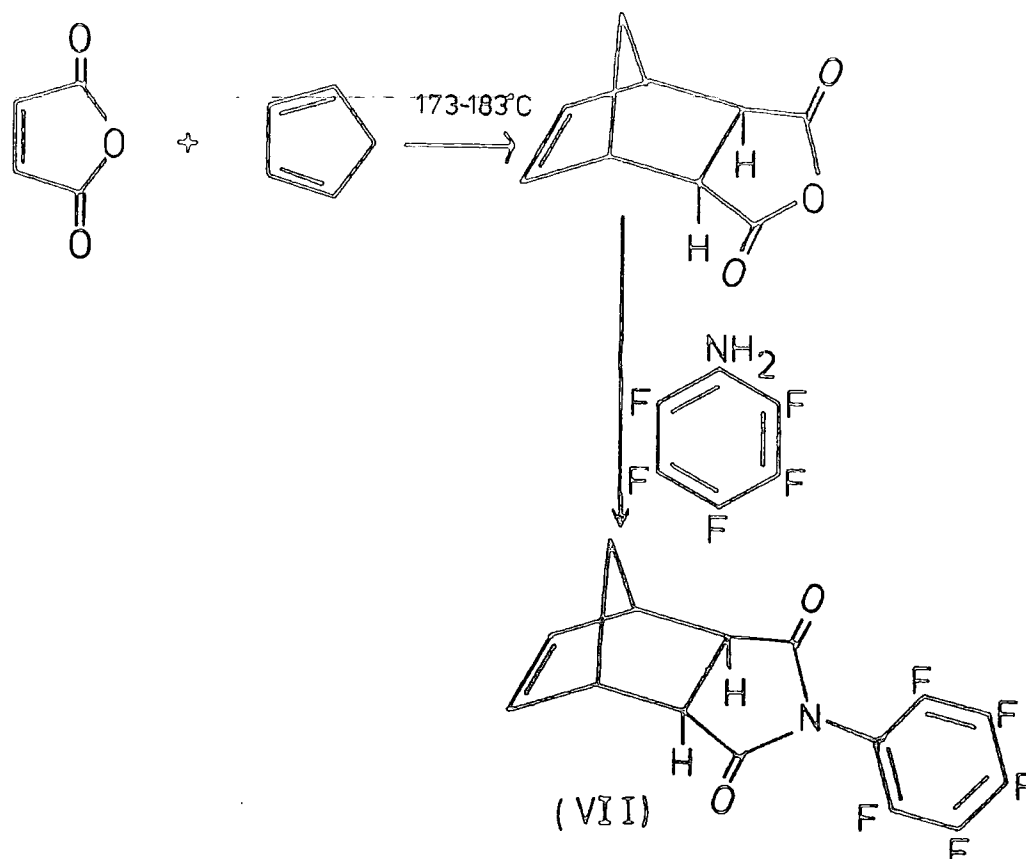


FIGURE 2.11 Synthesis of *exo*-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene, 2,3-dicarboximide

The Diels Alder reaction between cyclopentadiene and maleic anhydride was carried out at elevated temperature in order to optimise the yield of *exo* anhydride.<sup>140</sup> The *exo* anhydride was purified by successive recrystallisations from chlorobenzene; its infra-red spectrum was consistent with the expected product (Appendix B,9). Reaction of the *exo* anhydride with pentafluoroaniline in glacial acetic acid afforded the imide, VII. Monomer VII was recovered as a white crystalline solid with correct elemental analysis. The infra-red

of the product (Appendix B,10) showed characteristic bands due to olefinic C-H ( $3070\text{ cm}^{-1}$ ), carbonyl ( $1790\text{ cm}^{-1}$ ), CH=CH ( $1650\text{ cm}^{-1}$ ) and C-F ( $1300\text{ cm}^{-1}$ ). Its mass spectrum gave a typical breakdown pattern of a norbornene derivative, (Appendix C,6), with a base peak at 66 mass units arising from a retro Diels Alder reaction. The  $^{19}\text{F}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  nmr shifts and assignments are tabulated in Tables 2.8, 2.9 and 2.10 respectively.

TABLE 2.8  $^{19}\text{F}$  N.m.r. shifts of Monomer VII recorded at 56.45 MHz,  $\text{CFCl}_3$  external reference

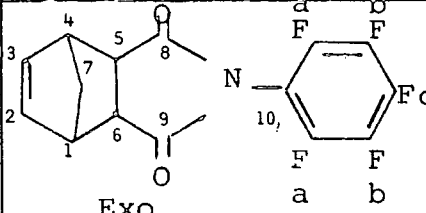
Compound	Shift/ ppm	Multiplicity	Inte- gral	Assign- ment
 Exo	161.7	m	2	b, b'
	151.4	t, $J_{cb} = 20.7\text{Hz}$	1	c
	143.3	d, $J_{ab} = 22.6\text{Hz}$	2	a, a'

TABLE 2.9  $^1\text{H}$  N.m.r. spectrum and Assignments of Monomer VII, recorded at 300.13MHz, TMS internal reference

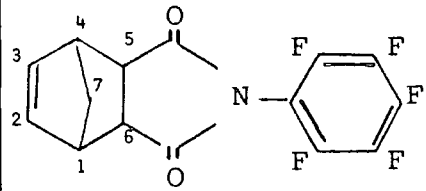
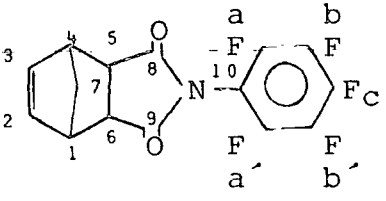
Compound	Shift/ ppm	Multiplicity	Inte- gral	Assign- ment
 Exo	6.36	Resolved into 3 lines separated by 1.76Hz	1	2, 3
	3.45	s	1	5, 6
	2.90	s	1	1, 4
	1.61	Abq, $\delta_A = 1.65$ , $\delta_B = 1.58$ , $J_{AB} = 10.1\text{Hz}$ , A limb split into doublets, $J, 1.4\text{Hz}$	1	7

TABLE 2.10  $^{13}\text{C}$  N.m.r. shifts and assignments of Monomer VII, recorded at 75.46 MHz, TMS internal reference

Compound	Shift/ ppm	Multiplicity	Assign- ment
 <p>Exo</p>	174.8	s	8,9
	144.7	d, $^1J_{\text{C-F}}=251\text{Hz}$	a, a'
	140.9	d, $^1J_{\text{C-F}}=257\text{Hz}$	c
	138.5	d, $^1J_{\text{C-F}}=254\text{Hz}$	b, b'
	137.9	s	2,3
	107.4	s	10
	43.1	s	7
	48.6	s	6,5
	45.9	s	1,4

The assignment of signals in the n.m.r. spectra follows in a routine manner. Low intensity signals observed in the spectra (not tabulated) are assigned to a small proportion of endo isomer present.

2.3 (b) Synthesis and Characterization of endo-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (VIII)

Endo-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide was prepared *via* the route depicted in Figure 2.12.

The Diels Alder reaction was carried out at low temperature ( $0-5^{\circ}\text{C}$ ) to yield endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyanhydride,<sup>141</sup> (infra-red spectrum, Appendix B,11). Reaction of the anhydride with pentafluoroaniline in glacial acetic acid gave the endo imide (VIII). The infra-red spectrum (Appendix B,12) and mass spectrum (Appendix C,6)



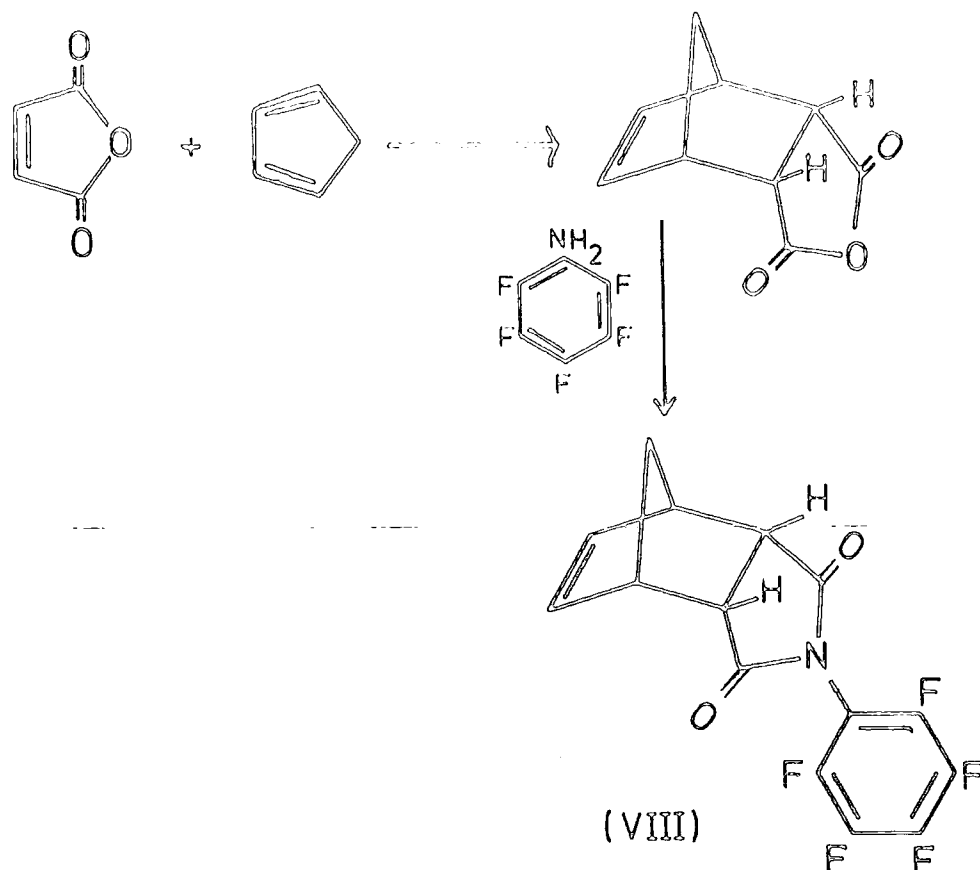


FIGURE 2.12 Synthesis of endo-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (VIII).

were similar to that obtained for the exo isomer. The  $^{19}\text{F}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. data for the adduct are tabulated in Tables 2.11, 2.12 and 2.13 respectively.

TABLE 2.11  $^{19}\text{F}$  N.m.r. shifts and assignments of Monomer VIII, recorded at 56.45 MHz,  $\text{CFCl}_3$  external reference

Compound	Shift/ ppm	Multiplicity	Integral	Assignment
<p style="text-align: center;">Endo</p>	161.5	d of d of d, $J_{ab}=20.7\text{Hz}$ $J_{bc}=20.7\text{Hz}$ , $J_{a'b}=5.6\text{Hz}$	2	b
	151.9	t, $J_{cb}=20.7\text{Hz}$	1	c
	143.3	d of d of d, $J_{a'b}=20.7\text{Hz}$ $J_{a'b}=5.6\text{Hz}$ , $J_{a'a}=5.6\text{Hz}$	1	a'
	141.2	d of d of d, $J_{ab}=20.7\text{Hz}$ $J_{ab}=5.6\text{Hz}$ , $J_{aa}=5.6\text{Hz}$	1	a

The ortho fluorines (a and a') give resonances at different positions indicating that they are not equivalent. Therefore, it seems that there are probably conformational preferences in this system, and that repulsion between the carbonyl groups and ortho fluorines results in a preferred conformation in which the plane of the ring is perpendicular to the plane of the carbonyl groups. The  $^{19}\text{F}$  n.m.r. of the exo adduct gave one doublet for the ortho fluorines, indicating that they were magnetically equivalent. It is possible that there is hindered rotation in both adducts, but the difference in environment of the ortho fluorines in the exo isomer is not sufficient to allow them to be resolved as separate signals, whereas in the endo case the environments are significantly different. This may be seen more clearly by consulting molecular models. The repulsion between the carbonyl group and the pentafluorophenyl ring would not be expected to be large and the barrier to rotation should be relatively easily overcome. However, variable temperature n.m.r. studies on both forms caused no apparent effect on the spectra.

Examination of the  $^{13}\text{C}$  n.m.r. data (Table 2.13) to determine if the ortho carbons gave separate resonances, was performed but the relevant signals could not be easily identified due to their low intensity. Hence, the explanation of the multiplicity observed in the  $^{19}\text{F}$  n.m.r. spectrum remains somewhat uncertain in detail although the structural assignment is unambiguous.

TABLE 2.12  $^1\text{H}$  N.m.r. Shifts and Assignments of Monomer (XIII) recorded at 300.13 MHz, TMS external reference

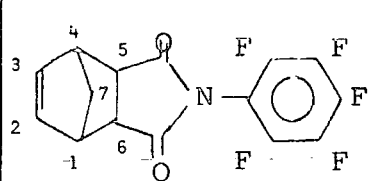
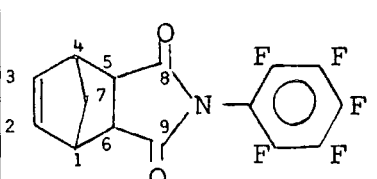
Compound	Shift/ ppm	Multiplicity	Integral	Assignment
 Endo	6.25	s	1	2,3
	3.54	d, $J_{1,6} = 1.5$ Hz	1	5,6
	3.51	d, $J_{1,6} = 1.5$ Hz	1	1,4
	1.63	ABq, $\delta_A = 1.72$ , $\delta_B = 1.55$ $J_{AB} = 8.8$ Hz	1	7

TABLE 2.13  $^{13}\text{C}$  N.m.r. Shifts and Assignments of Monomer (XIII) recorded at 75.46 MHz, TMS internal reference

Compound	Shift/ ppm	Multiplicity	Assignment
	174.5	s	8,9
	143.7	d, $^1J_{\text{C-F}} = 256$ Hz	a, a'
	142.2	d, $^1J_{\text{C-F}} = 256$ Hz	c
	138.0	d, $^1J_{\text{C-F}} = 255$ Hz	b, b'
	134.9	s	2,3
	107.3	s	10
	52.2	s	7
	46.9	s	6,5
45.6	s	1,4	

### 2.9 Synthesis and Characterization of 5-perfluorohexyl bicyclo[2.2.1]hept-2-ene (IX)

Cyclopentadiene and 1H,1H,2H-perfluoro-oct-1-ene react at 130°C to give a mixture of exo and endo isomers of 5-perfluorohexyl bicyclo[2.2.1]hept-2-ene as the major product, as shown in Figure 2.13.

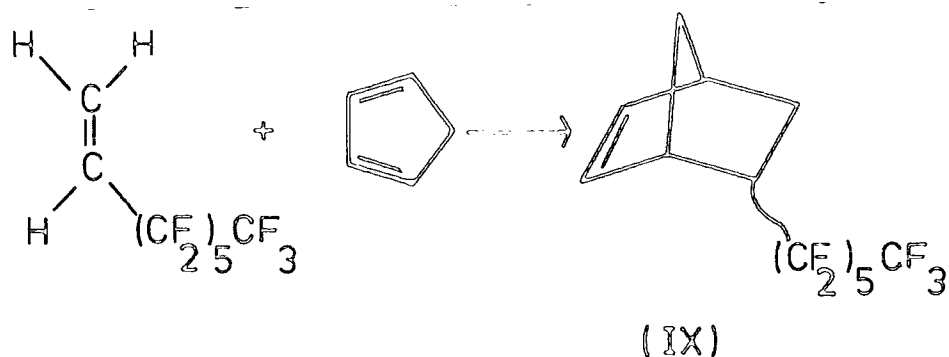


FIGURE 2.13 Synthesis of 5-perfluorohexyl bicyclo[2.2.1]-hept-2-ene

The ratio of exo and endo isomers formed in the mixture was determined using  $^{19}\text{F}$  n.m.r. spectroscopy; the endo content was 75%. The shifts and assignments are given in Table 2.14.

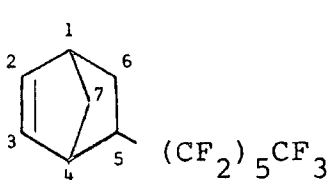
TABLE 2.14  $^{19}\text{F}$  N.m.r. Shifts and Assignments of Monomer (IX), recorded at 56.45MHz,  $\text{CFCl}_3$  Internal Standard

Compound	Shift/ppm	Multiplicity	Integral	Assignment
	127.3	broad s	2	b, c, d, e
	123.3	" "	6	
	115.0	" "	0.5	a, exo
	113.5	" "	1.5	a, endo
	80.8	" "	3	f

The assignment of the  $^{19}\text{F}$  n.m.r. is based on the assumption that the endo adduct is formed in the greater proportion, and as expected the endo resonance appears at lower field than the exo adduct signal (see earlier discussions).

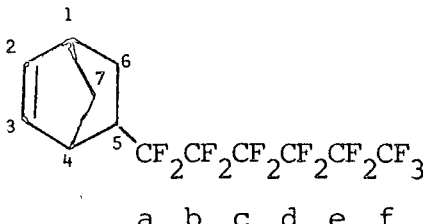
The  $^1\text{H}$  n.m.r. of the mixture was run at 360.13MHz, but was extremely complex, and defied a thorough interpretation. However, the shifts of the centres of multiple signals are given in Table 2.15, and the ratio of the integrals for the vinyl, methylene and methine signals is consistent with a bicyclo[2.2.1]hept-2-ene derivative.

TABLE 2.15  $^1\text{H}$  N.m.r. Shifts and Assignments of Monomer (IX), recorded at 360.13MHz, TMS Internal reference

Compound	Shift/ ppm	Multiplicity	Integral	Assignment
	6.1	m	)	3,2
	5.9	m	)	
	3.1	broad s	)	5,4,1
	2.9	" "	)	
	2.8	m	)	
	2.0	m	)	4
	1.5	m	)	
	1.4	m	)	
	1.3	m	)	

The  $^{13}\text{C}$  N.m.r. shifts and assignments are given in Table 2.16.

TABLE 2.16  $^{13}\text{C}$  N.m.r. Shifts and Assignments of Monomer (IX), recorded at 90.56 MHz.

Compound	Shift/ ppm	Multi- plicity	Integral	Assignment
 <p> <math>\text{CF}_2^a\text{CF}_2^b\text{CF}_2^c\text{CF}_2^d\text{CF}_2^e\text{CF}_3^f</math> </p>	138.3	s	1	3, exo
	137.2	s	3	3, endo
	136.4	s	-1	2, exo
	131.8	s	3	2, endo
	105-115	m	-	a - f
	49.6	s	3	7, endo
	46.4	s	1	7, exo
	43.7	s	3	1 or 4 endo
	42.5	s	1	1 or 4 exo
	42.1	s	3	1 or 4 endo
	41.3	s	1	1 or 4 exo
	40.7	s	1	5, exo
	40.5	t	3	5, endo
	27.5	s	3	6, endo
26.7	s	1	6, exo	

The relative intensity of signals in the  $^{13}\text{C}$  n.m.r. spectrum allows resonances due to exo and endo isomers to be differentiated. In the vinyl region, carbons 2 and 3 are distinguished on the basis that the long perfluoroalkyl chain is more likely to interact with carbon 3, causing a downfield shift for this signal. The methylene and methine signals may be distinguished with the aid of a DEPT spectrum (Distortionless Enhancement by Polarisation) (see Chapter Three) in which  $-\text{CH}-$  signals appear as positive peaks and  $-\text{CH}_2-$  resonances as negative peaks. The triplet multiplicity of

the signal at 40.5 ppm allows this resonance to be assigned to carbon 5, the multiplicity being a consequence of its coupling to the  $\alpha$  fluorines. It was not possible to make an unambiguous assignment of the shifts for  $C_1$  and  $C_4$ .

The methylene carbons are assigned by comparing the spectrum with that of 2,3 bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene. The  $C_7$  resonances are likely to be observed in similar positions ( $\sim 50$  ppm) and therefore the signals at 27.5 and 26.7 ppm are attributed to carbon 6.

The infra-red spectrum (Appendix B,13) and mass spectrum (Appendix C,7) were consistent with the structure assigned.

#### 2.10 Synthesis and Characterization of 5-perfluorooctyl bicyclo[2.2.1]hept-2-ene (X)

The Diels Alder reaction between cyclopentadiene and 1H,1H,2H-perfluorodec-1-ene gave 5-perfluorooctyl bicyclo[2.2.1]hept-2-ene (X) as a mixture of exo and endo isomers, (Figure 2.14).

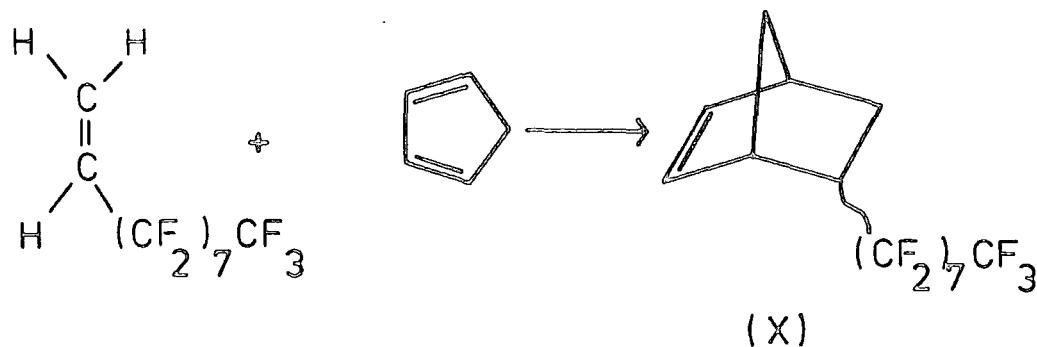
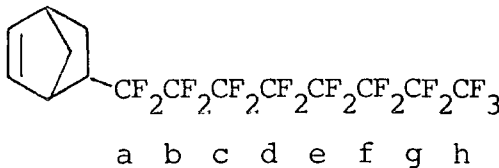


FIGURE 2.14 Diels Alder reaction between cyclopentadiene and 1H,1H,2H-perfluorodec-1-ene

The  $^{19}\text{F}$  N.m.r. shifts and assignments are given in Table 2.17.

TABLE 2.17  $^{19}\text{F}$  N.m.r. shifts and assignments of Monomer (X) recorded at 56.45MHz,  $\text{CFCl}_3$  internal reference.

Compound	Shift/ ppm	Multiplicity	Integral	Assignment
	127.9	broad s	14	b,c,d,e,f,g
	121.2	m		
	115.3	m	0.5	a, exo
	113.8	broad s	1.5	a, endo
	81.6	t	3	h

The ratio of exo to endo isomers formed from the reaction was 25:75.

The  $^1\text{H}$  n.m.r. was complex, and not interpreted in detail. The shifts and assignments of the centres of multiple bands are given in Table 2.18.

The  $^{13}\text{C}$  n.m.r. may be assigned by analogy with the spectrum of 5-perfluorohexyl bicyclo[2.2.1]hept-2-ene. The shifts and assignments are given in Table 2.19.

The infrared (Appendix B14) and mass spectrum (Appendix C8) were consistent with the assigned structure.



TABLE 2.18  $^1\text{H}$  N.m.r. Shifts and Assignments of Monomer (X),  
recorded at 360.13MHz, TMS internal standard

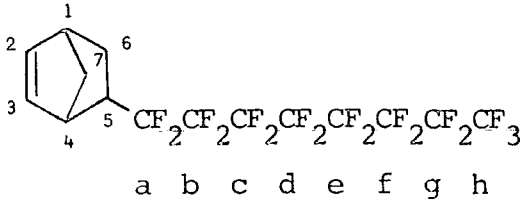
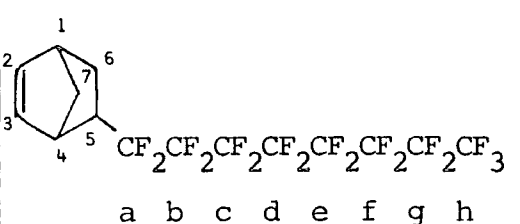
Compound	Shift/ ppm	Multi- plicity	Integral	Assign- ment
 <p>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100</p>	6.1	m	2	2,3
	5.9	m		
	3.1	broad s	3	1,4,5
	3.0	broad s		
	2.9	broad s		
	2.7	broad s		
	1.9	m		
	1.5	s		
	1.4	m	4	6,7
	1.3	m		
	1.3	m		
	1.2	m		

TABLE 2.19  $^{13}\text{C}$  N.m.r. Shifts and Assignments of Monomer (X),  
recorded at 90.56 MHz, TMS internal standard

Compound	Shift/ ppm	Multi- plicity	Integral	Assign- ment
 <p>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100</p>	138.3	s	1	3,exo
	137.2	s	3	3,endo
	136.4	s	1	2,exo
	131.8	s	3	2,endo
	105-125	m	-	a,b,c,d,e,f,g,h
	49.6	s	3	7,endo
	46.3	s	1	7,exo
	43.7	s	3	4,endo
	42.5	s	1	4,exo
	42.1	s	3	1,endo
	41.3	s	1	1,exo
	41.2	s	1	5,exo
	40.5	t	3	5,endo
	27.5	s	3	6,endo
	26.7	s	1	6,exo

EXPERIMENTAL

2.11 (a) Reagents

3,3,4,4-Tetrafluoro-4-bromobut-1-ene, 1H,1H,2H-perfluorodec-1-ene, and 1H,1H,2H-perfluorooct-1-ene were purchased from Riedel de Haën, trifluoroprop-1-ene was purchased from Fluorochem, and all other fluoroalkenes and fluoroalkynes were purchased from Bristol Organics. Fluorocarbons were used as supplied. N,N-dimethylacetamide was purchased from BDH Chemicals Ltd., and fractionally distilled before use. Cyclopentadiene was freshly prepared by thermal cracking of dicyclopentadiene<sup>132</sup> which was purchased from Koch Light.

(b) Preparation of 3,3,3-trifluoropropyne (with PCT)

N,N-Dimethylacetamide was fractionally distilled at 164-166°C onto activated molecular sieve (4Å). A 3-neck round-bottomed flask was fitted with a mechanical stirrer, condenser, thermometer and pressure equalising dropping funnel. The apparatus was purged with nitrogen, *via* an inlet on the stirrer gland, before use and a nitrogen pressure was maintained throughout the experiment. Two traps, immersed in liquid air were connected to the top of the condenser. N,N-Dimethylacetamide (300 cm<sup>3</sup>), zinc (36.0g, 554 mmol) and zinc chloride (3.4g, 25 mmol) were added to the flask, and the mixture heated with stirring to 100°C, 1,1,2-Trichloro-3,3,3-trifluoropropene (50.0g, 250 mmol) was added carefully *via* the dropping funnel, so as to maintain a temperature of 95-100°C. The reaction mixture was allowed to cool to 60°C and water (100 cm<sup>3</sup>) was added dropwise at a rate which maintained the temperature at 60°C. When the addition of water

was complete the reaction mixture was heated to 80-85°C for 2 hours. A gaseous product was evolved slowly, which was collected in the cold traps, and then distilled under reduced pressure into a preweighed metal can. The product was identified as 3,3,3-trifluoropropyne (16.0g, 170 mmole, 68%) with correct i.r. spectrum,  $\nu_{\max}$  3320  $\text{cm}^{-1}$ , 2150  $\text{cm}^{-1}$  and 1250-1150  $\text{cm}^{-1}$ .

(c) Reaction of Cyclopentadiene with a fluoroalkene or fluoroalkyne

(i) General Procedure

In cases where the fluoroalkene was a liquid, a known volume was injected into a Pyrex Carius tube containing a small quantity of hydroquinone, and degassed. The required amount of cyclopentadiene was injected into a separate flask, degassed, and condensed into the Carius tube by vacuum transfer. When the fluoroalkyne or fluoroalkene was gaseous, a known volume was condensed into the Carius tube, followed by the required volume of cyclopentadiene. The tube was sealed under vacuum and placed in a furnace at the appropriate temperature for the required time. After cooling to room temperature the tube was removed from the furnace, cooled in liquid air, and the seal broken by hot spotting. The products were recovered and distilled.

(ii) 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene(I)

Cyclopentadiene (6.4g, 97 mmoles), hexafluorobut-2-yne (15.7g, 97 mmoles) and hydroquinone (0.05g) were sealed *in vacuo* and left at room temperature for 24 hours to give:

(i) 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (I) (20.3g, 89 mmole, 92%); B.p. 120-122°C; with correct i.r.

spectrum, (ii) a trace of dicyclopentadiene and polyadducts.

(iii) 2-Trifluoromethyl bicyclo[2.2.1]hepta-2,5-diene(II)  
(with P.C.T.).

Cyclopentadiene (10.7g, 163 mmoles), 3,3,3-trifluoropropyne (15.3g, 163 mmoles) and hydroquinone (0.05g) were sealed *in vacuo* and heated at 155°C for 65 hours to give: (i) 2-trifluoromethyl bicyclo[2.2.1]hepta-2,5-diene (II) (20.0g, 125 mmoles, 77%); b.p. 108°C; [Found: C, 60.5; H, 4.6; F, 36.0%; C<sub>8</sub>H<sub>7</sub>F<sub>3</sub> requires C, 60.00; H, 4.4; F, 35.6%]; m/e 160 (M<sup>+</sup>); with correct i.r.; (ii) dicyclopentadiene and polyadducts.

(iv) Exo and Endo-5-trifluoromethyl bicyclo[2.2.1]hept-2-ene

Cyclopentadiene (8.0g, 121 mmoles), 3,3,3-trifluoropropene (11.6g, 121 mmoles) and hydroquinone (0.05g), were sealed *in vacuo* and heated to the required temperature for the required time (see Table 2.3) to give: (i) exo and endo-5-trifluoromethyl bicyclo[2.2.1]hept-2-ene (III) and (IV); b.p. 120°C; with correct infra-red spectrum, (ii) dicyclopentadiene and polyadducts.

(v) 5-Pentafluorophenyl bicyclo[2.2.1]hept-2-ene

Cyclopentadiene (1.7g, 26 mmole), pentafluorostyrene (5g, 26 mmole), and hydroquinone (0.05g) were sealed *in vacuo* and heated at 140°C for 48 hours to give: (i) 5-pentafluorophenyl bicyclo[2.2.1]hept-2-ene (VI) (5.6g, 22 mmole, 84%); b.p. 182-185°C; [Found: C, 60.4; H, 3.4; C<sub>13</sub>H<sub>9</sub>F<sub>5</sub> requires C, 60.0; H, 3.4] m/e 260 (M<sup>+</sup>),  $\nu_{\max}$  3030 cm<sup>-1</sup> (vinyl C-H), 2970 cm<sup>-1</sup> (C-H stretch), 1470 cm<sup>-1</sup> (C-F).

(vi) 5-(2-Bromotetrafluoroethyl) bicyclo[2.2.1]hept-2-ene

Cyclopentadiene (8.0g, 121 mmoles), 3,3,4,4-tetrafluoro-4-bromobut-1-ene (25.0g, 121 mmoles), and hydroquinone were sealed *in vacuo* and heated at 160°C for 72 hours to give:

(i) 5-(2-bromotetrafluoroethyl bicyclo[2.2.1]hept-2-ene (V), (27.4g, 100 mmole, 83%); b.p. 184-186°C; [Found, C, 39.8; H, 3.4; C<sub>9</sub>H<sub>9</sub>F<sub>4</sub>Br requires C, 39.6; H, 3.3], M(mass spectrometry) 273;  $\nu_{\max}$  3060 cm<sup>-1</sup> (vinyl C-H stretch), 3970 cm<sup>-1</sup> (C-H stretch), 1100 cm<sup>-1</sup> (C-F).

(vii) 5-Perfluorohexyl bicyclo[2.2.1]hept-2-ene

Cyclopentadiene (3g, 45 mmole), 1H,1H,2H-perfluorooct-1-ene (15.8g, 46 mmole), and hydroquinone (0.05g) were sealed *in vacuo*, and heated at 150°C for 72 hours to give:

(i) 5-perfluorohexyl bicyclo[2.2.1]hept-2-ene (IX), (15.8g, 38 mmole, 84%); b.p. 60-68°C at 6 x 10<sup>-2</sup> mmHg; [Found: C, 37.9; H, 1.9; C<sub>13</sub>H<sub>9</sub>F<sub>13</sub> requires C, 37.9; H, 2.2]. Mass (mass spectrometry) 412; i.r.  $\nu_{\max}$  3030 cm<sup>-1</sup> (vinyl C-H stretch), 2980 cm<sup>-1</sup> (C-H stretch) and 1200 cm<sup>-1</sup> (C-F).

(viii) 5-Perfluorooctyl bicyclo[2.2.1]hept-2-ene

Cyclopentadiene (2.5g, 37 mmoles), 1H,1H,2H-perfluorodec-1-ene (16.7g, 37 mmole) and hydroquinone (0.05g) were sealed *in vacuo* and heated at 150°C for 72 hours to give: 5-perfluorooctyl bicyclo[2.2.1]hept-2-ene (17g, 33 mmole, 89%), b.p. 78-80°C at 6x10<sup>-3</sup> mmHg; [Found: C, 35.4, H, 1.7; C<sub>15</sub>H<sub>9</sub>F<sub>17</sub> requires C, 35.1; H, 1.7; F, 63.0]; Mass (Mass spectrometry) m/e 492 (m-20, HF), i.r.  $\nu_{\max}$  3035 cm<sup>-1</sup> (vinyl C-H stretch), 2980 cm<sup>-1</sup> (C-H stretch) and 1220 cm<sup>-1</sup> (C-F).

(d) Synthesis of Exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride

A 500 cm<sup>3</sup> 3-neck round-bottomed flask was fitted with a condenser, thermometer and dropping funnel. Maleic anhydride (88.1g, 0.9 mole) and 1,2-dichlorobenzene (100 cm<sup>3</sup>) were added to the flask and the solution heated to 173°C. Dicyclopentadiene (59.4g, 0.45 mole) was added to the flask *via* the dropping funnel over a period of 2 hours. The mixture was then heated to reflux (183-187°C) for 1½ hours. The flask was allowed to cool overnight and the solid product recrystallised several times from chlorobenzene to give exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride (88.5g, 0.5 mole, 60%); m.pt. 130°C, lit.<sup>142</sup> 143°C (100% exo) 130°C (87% exo).

(e) Synthesis of Endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride

A 1 litre, 3-neck round-bottomed flask was fitted with a thermometer, condenser, a serum cap and a magnetic follower. Maleic anhydride (62.8g, 0.64 moles) and anhydrous diethyl ether (400 cm<sup>3</sup>) were added to the flask and stirred. The solution was cooled in an ice/salt bath between 0° and 5°C. Cyclopentadiene (42.2g, 0.64 moles) was added dropwise *via* the serum cap, using a syringe; the temperature of the solution was not allowed to rise above 10°C during the addition. The mixture was stirred with cooling for a further 2 hours, after which the ice bath was removed and the flask left overnight. The product, endo-bicyclo[2.2.1]hept-5-ene, 2,3-dicarboxy anhydride (58.8g, 0.36 mole, 56%), m.pt. 160°C, Lit.<sup>142</sup>, 165°C was precipitated as a white crystalline solid which was subsequently used without further purification.

(f) Synthesis of exo-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide(VII)

Exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride (15.2g, 0.09 moles) in glacial acetic acid (70 cm<sup>3</sup>) and pentafluoroaniline (17g, 0.09 moles) in glacial acetic acid (20 cm<sup>3</sup>) were mixed together in a 250 cm<sup>3</sup> round-bottomed flask, and heated to reflux for 2 hours. (The solution changed colour during this period from a pale yellow to a deep orange). The solution was allowed to cool and the product precipitated by the dropwise addition of water. The product was filtered off and recrystallised several times from a 50:50 mixture of acetic acid and water. The product was a white crystalline solid identified as exo-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (VII); (18.9g, 0.058 moles, 64%); m.p. 116°C; [Found, C, 54.6; H, 2.2; N, 3.9; F, 28.4; C<sub>15</sub>H<sub>8</sub>F<sub>5</sub>NO<sub>2</sub> requires C, 54.7; H, 2.4; N, 4.2; F, 28.5]; m/e 329 (M<sup>+</sup>);  $\nu_{\max}$ , 3060 cm<sup>-1</sup> (vinyl C-H stretch), 3000 (C-H stretch), 1790 cm<sup>-1</sup> (CO-N-CO) and 1300 cm<sup>-1</sup> (C-F).

(g) Synthesis of endo-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide(VIII)

Endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride (8.6g, 0.05 moles) in glacial acetic acid (40 cm<sup>3</sup>) and pentafluoroaniline (9.5g, 0.05 moles) in glacial acetic acid (10 cm<sup>3</sup>) were mixed together in a 100 cm<sup>3</sup> round-bottomed flask and heated to reflux for 2 hours. The solution was allowed to cool and the product recovered in the same way as the exo adduct (see (f)). The product was a white crystalline solid which was identified as endo-N-pentafluorophenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide(VIII); (10.5g, 0.032 moles, 64%); m.p. 133°C; [Found: C, 54.8; H, 2.3; N, 3.9; F, 29.0;



$C_{15}H_8F_5NO_2$  requires, C, 54.7; H, 2.4; N, 4.2; F, 28.5];  
 m/e 329 ( $M^+$ );  $\nu_{max}$  3050  $cm^{-1}$  (vinyl C-H stretch), 1780 and  
 1720 (CO-N-CO-), 1300  $cm^{-1}$  (C-F).

(h) Attempted Synthesis of Endo-5-trifluoromethyl bicyclo[2.2.1]hept-2-ene

(i) Synthesis of 5-carboxyl bicyclo[2.2.1]hept-2-ene

It is important to conduct all the following operations in a fumes cupboard since the product has an obnoxious and lingering odour. A 3-neck 250  $cm^3$  round-bottomed flask was fitted with a pressure equalising dropping funnel, thermometer, reflux condenser, drying tube, and magnetic follower. Acrylic acid (40.3g, 0.6 moles) was added to the flask, which was surrounded by an ice bath. Freshly distilled cyclopentadiene (40.1g, 0.6 moles) was added to the flask, with stirring, *via* the dropping funnel. The addition was complete in 2 hours, and the flask left to stand at room temperature overnight. The resulting product was basified with 2M NaOH, washed with ether (3x100  $cm^3$ ) and the aqueous layer collected. The aqueous layer was acidified with 2M HCl and the liberated acid extracted with ether (3x200  $cm^3$ ). The combined ether extracts were dried ( $MgSO_4$ ) and evaporated to yield the crude product as a pale yellow viscous liquid. This was used without any further purification for the next stage.

(ii) Synthesis of the iodolactone of 5-carboxynorbornene

5-Carboxy-bicyclo[2.2.1]hept-2-ene (6.2g, 45 mmole) and sodium bicarbonate (6.3g, 75 mmole) in water (150  $cm^3$ ) were placed in a 500  $cm^3$  round-bottomed flask. A solution of iodine (12.7g, 50 mmole) and potassium iodide (17.4g,

104 mmole) in water (75 cm<sup>3</sup>) was added, and the resulting mixture placed in the dark for 12 hours. The aqueous layer was decanted from the resultant black oil, and the oil dissolved in chloroform (50 cm<sup>3</sup>). Aqueous sodium thiosulphate (~0.2M) was added slowly to the chloroform solution with vigorous shaking, until both layers were colourless. The aqueous layer was further extracted with chloroform (2x50 cm<sup>3</sup>) and the combined chloroform extracts washed with saturated aqueous sodium bicarbonate (100 cm<sup>3</sup>) and brine (100 cm<sup>3</sup>), and dried (MgSO<sub>4</sub>). The chloroform was evaporated to yield the iodolactone, which was recrystallised from ethanol to give the product as white needles (9.6g, 36.3 mmole, 80%).

(iii) Attempted fluorination of 5-carboxy bicyclo[2.2.1]-hept-2-ene

5-Carboxy bicyclo[2.2.1]hept-2-ene (5.65g, 0.04 moles) was placed in a metal tube, and the valve fitted. Sulphur tetrafluoride (14g, 0.13 moles) was transferred *in vacuo* into the tube, and the valve closed. The tube was placed in a rocking autoclave at 80°C for 8 hours. After cooling to room temperature, excess sulphur tetrafluoride was vented into an ice cold sodium bicarbonate solution. The valve was removed and the contents of the tube recovered. The product was a black tar from which no volatile organofluorine products could be recovered.

CHAPTER THREE

POLYMERIZATION OF

2,3-BIS (TRIFLUOROMETHYL) NORBORNADIENE,

2-TRIFLUOROMETHYLNORBORNADIENE,

AND EXO AND ENDO-5-TRIFLUOROMETHYLNORBORNENE

### 3.1 Nomenclature

Norbornene and norbornadiene are the trivial names for the bicyclo[2.2.1]hept-2-enes and hepta-2,5-dienes described in Chapter Two. When naming the polymers derived from these monomers it is more convenient to use the trivial names rather than the more correct, but rather awkward systematic nomenclature. Hence, the polymer derived from 5-pentafluorophenylnorbornene is called poly(5-pentafluorophenyl norbornene) rather than poly(4-pentafluorophenyl-1,3-cyclopentylene vinylene).

### 3.2 Background

The ring opening metathesis polymerization of substituted norbornenes and norbornadienes is well established.<sup>8</sup> Previous workers in the field have demonstrated that fluorinated norbornenes can be tolerated by some metathesis catalysts.<sup>83-90</sup> The polymers prepared appeared to have highly disordered microstructures and were amorphous materials. Nevertheless, their results encouraged the belief that stereoregular polymers would be accessible *via* this approach. This chapter is concerned with an investigation into the polymerization of monomers I, II, III and IV. An attempt has been made to establish the microstructure of the polymer chains using <sup>13</sup>C n.m.r. and infrared spectroscopy. The interpretation of the data obtained from these analytical techniques is described in Section 3.3.

### 3.3 Analytical Methods

#### (a) Infrared spectroscopy

For organic polymers functional group analysis procedures are usually the same as for other organic molecules. Infrared active groups along the chain absorb as if each were a localised group in a simple molecule. Infrared spectroscopy is therefore used for identification purposes. The principle characteristic bands for these polymers are the vinyl CH stretch ( $3100-3000\text{ cm}^{-1}$ ),  $-C=C-$  stretch ( $1680-1620\text{ cm}^{-1}$ ) and C-F stretching modes ( $1400-1000\text{ cm}^{-1}$ ). In addition infrared spectroscopy can be used to elucidate certain aspects of polymer microstructure such as branching,<sup>143</sup> crystallinity<sup>144</sup> and *cis/trans* isomerism. In this work it has proved useful in determining the relative abundance of *cis/trans* double bonds in ring opened polymers; the C-H out of plane deformation for a *trans* unit generally occurs in the range  $980-960\text{ cm}^{-1}$ , and for a *cis* unit in the range  $730-665\text{ cm}^{-1}$ . In favourable cases these bands are distinct from other absorptions in the spectrum.

The infrared spectra of the polymers were recorded from free standing films cast from volatile solvents.

#### (b) Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance is probably the most powerful analytical technique for studying the microstructure of polymer chains. In the early 1960s proton n.m.r. was used to elucidate the microstructure of poly(methylmethacrylate) prepared *via* different polymerization procedures.<sup>145</sup> However, the overlap of signals in the n.m.r. of polymers such as

polypropylene led to ambiguous results.<sup>146</sup> Many of the difficulties encountered in proton n.m.r. are avoided in  $^{13}\text{C}$  n.m.r.<sup>147,148</sup> It is found that the chemical shift range is much larger than in  $^1\text{H}$  n.m.r., the natural abundance of  $^{13}\text{C}$  nuclei is 1.11% and spin-spin interactions between adjacent nuclei are very infrequent and can be neglected, and  $^1\text{H}$ - $^{13}\text{C}$  interactions can be eliminated by broad band decoupling. Coupling between  $^{19}\text{F}$  and  $^{13}\text{C}$  nuclei is much more difficult to eliminate and in this work is always present; in many respects this can be advantageous allowing carbons bonded either directly to fluorine or  $\alpha$  to fluorine atoms to be identified by the observed  $^{19}\text{F}$ - $^{13}\text{C}$  coupling constants, which are large and quite characteristic. In addition, it was anticipated that the fluorine substituents in different stereochemical environments would produce relatively large effects on  $^{13}\text{C}$  n.m.r. shifts, which also turns out to be the case.

The interpretation of  $^{13}\text{C}$  n.m.r. spectra is complicated since chemical shifts can be affected by subtle changes in microstructure. When assigning spectra it is necessary to take account of the following features of the microstructure, which may affect the number of resonances observed for a particular carbon.<sup>149-155</sup>

(i) Cis/trans double bonds

The shift of a particular carbon nucleus is sensitive to the stereochemistry of not only the nearest but also the next nearest double bond, and in some cases to double bonds which are even further removed. Hence, for the atactic polymer of norbornene depicted in Figure 3.1, we would expect to

see at least four signals for the allylic carbons corresponding to the *tt*, *tc*, *ct* and *cc* environments, where the first letter denotes the stereochemistry of the nearest double bond, and the second letter denotes the geometry of the next nearest double bond.

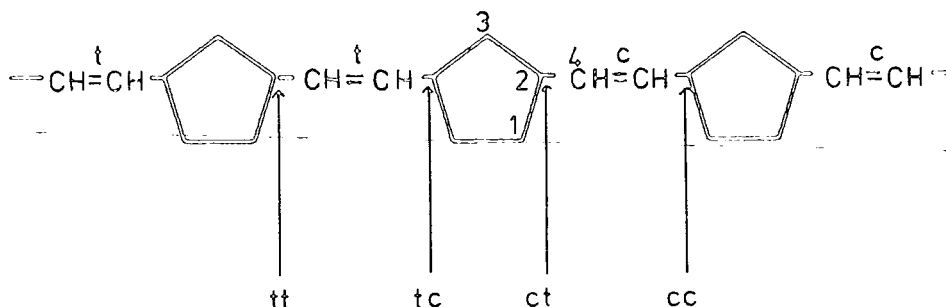


FIGURE 3.1 Cis/trans environments for the allylic carbons in poly(norbornene)

The relative intensities of the lines in the resolved multiplets in the  $^{13}\text{C}$  n.m.r. spectrum can be used to calculate the ratio of *cis/trans* unsaturation in the polymer. Using the formulae given below, the fraction of *cis* unsaturation ( $\sigma_c$ ) can be calculated from the integral of the appropriate signals (corresponding to the carbon labelling in Figure 3.1).

$$\sigma_c = \frac{c_4}{c_4 + t_4}$$

$$\sigma_c = \frac{ct_1 + cc_1}{tt_1 + tc_1 + ct_1 + cc_1}$$

$$\sigma_c = \frac{ct_2 + cc_2}{tt_2 + tc_2 + ct_2 + cc_2}$$

$$\sigma_c = \frac{cc_3 + 0.5(ct_3 + tc_3)}{(tc_3 + ct_3) + cc_3 + tt_3}$$

[Note for  $C_3$   $ct \equiv tc$ ]

(ii) Head/tail effects

When the monomer is unsymmetrically substituted head/tail effects are introduced into the polymer chain, (see Section 1.8(ii)). The  $^{13}\text{C}$  n.m.r. shift of a particular carbon nucleus is sensitive to the orientation of the nearest and next nearest substituent. Hence, ignoring the presence of potential complications from meso/racemic effects, for all *trans* atactic poly(5-trifluoromethylnorbornene) we would expect to see 2 signals for carbon 3 (see Figure 3.2 for numbering) corresponding to the HT and HH environments, as shown in Figure 3.2. Similarly, at least 2 signals would be expected for carbon 2, corresponding to the TT and TH environments.

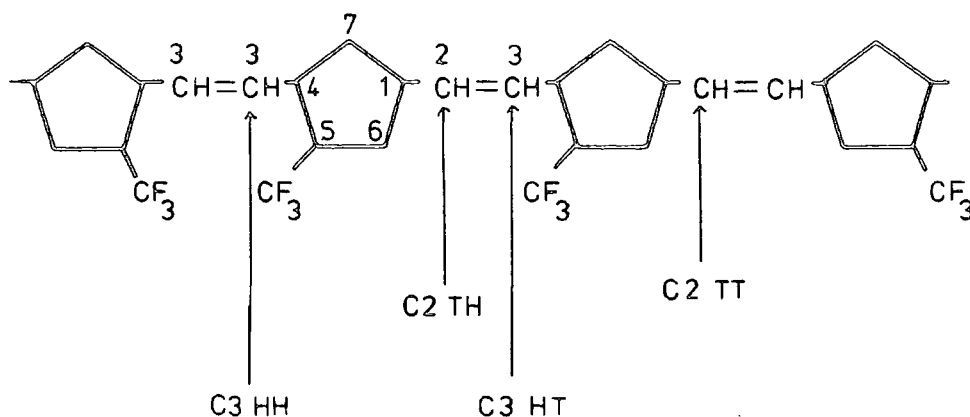


FIGURE 3.2 Head/Tail Effects in poly(5-trifluoromethyl-norbornene)

(iii) Meso/racemic effects

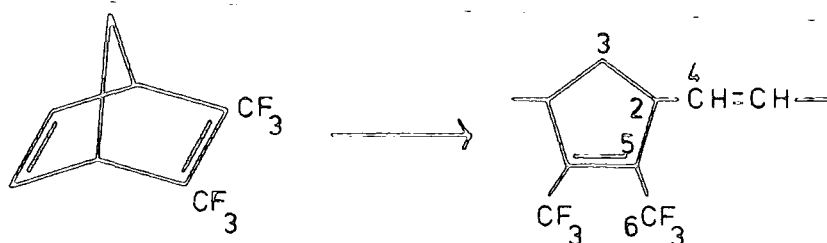
In some cases, separate signals may be resolved for certain carbon resonances depending on whether the dyad has an *m* or *r* configuration (see Section 1.8(iii)).



### 3.4 Polymerization of 2,3-bis(trifluoromethyl)norbornadiene(I)

#### (a) Interpretation of the $^{13}\text{C}$ n.m.r. spectrum

2,3-Bis(trifluoromethyl)norbornadiene has been polymerized previously using  $\text{WCl}_6/\text{Me}_4\text{Sn}$  as catalyst and the structure of the polymer proved to be the product of ring opening at the unsubstituted double bond.<sup>88</sup>



The distribution of *cis* and *trans* double bonds was found to be 54:46. Since the proportion of *cis* double bonds was so close to 50% there was some uncertainty about which signals corresponded to carbons associated with *cis* double bonds, and those associated with *trans* double bonds. In this work polymers of (I) with a range of  $\sigma_{\text{C}}$  values have been obtained allowing signals in the spectrum to be assigned with more confidence.

Monomer (I) is the simplest bicyclic alkene considered during the course of this work. The use of this symmetrically substituted monomer eliminates potential complication in the polymer derived from it, due to exo/endo isomerism and head-head-tail-tail and head-tail placements. Thus monomer (I) is likely to give a polymer with a relatively simple  $^{13}\text{C}$  n.m.r. spectrum.

The spectrum of poly(bis(trifluoromethyl)-norbornadiene) derived *via*  $\text{RuCl}_3$  catalysis is shown in Figure 3.3. This

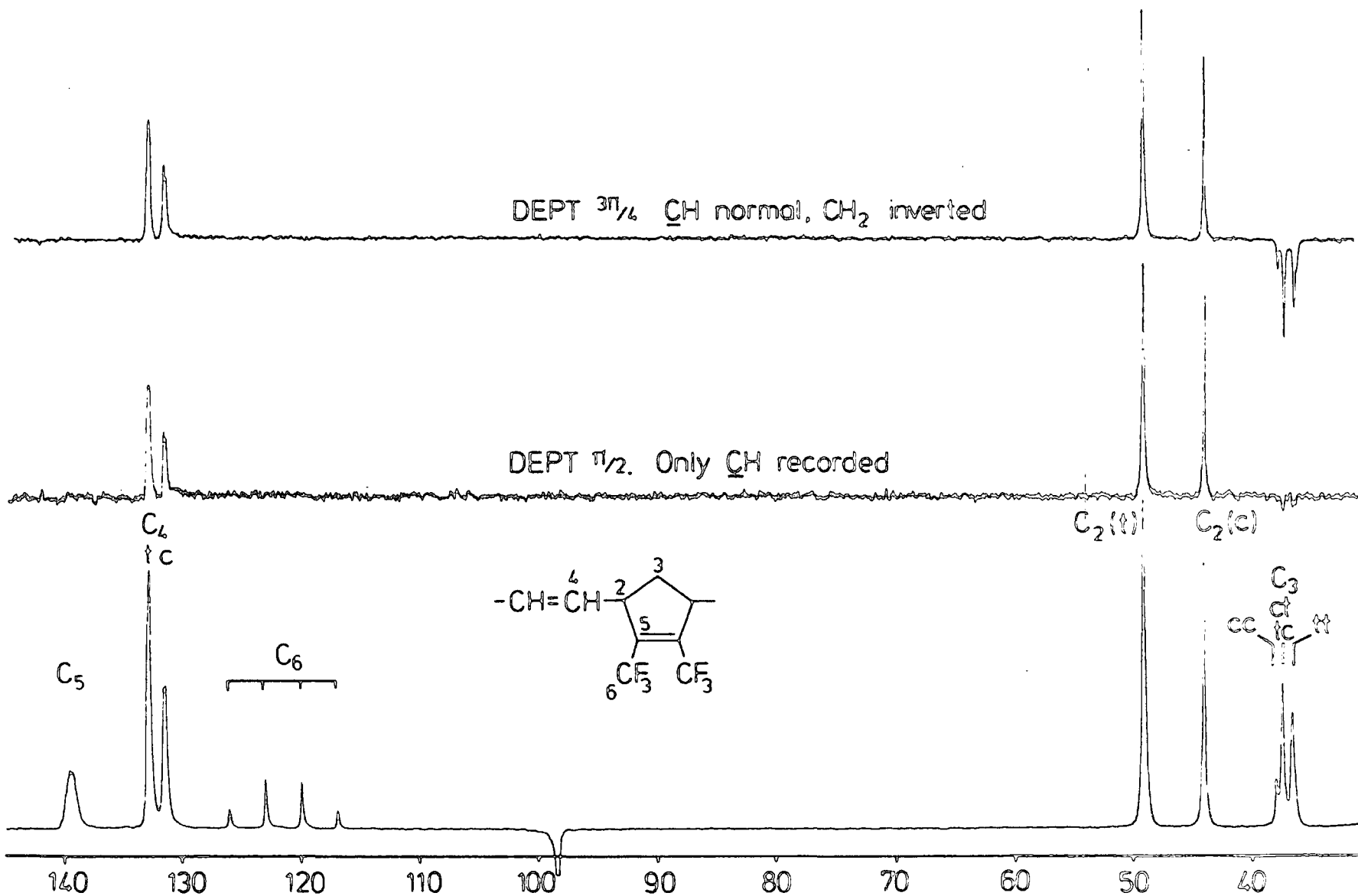


FIGURE 3.3  $^{13}\text{C}$  N.m.r. spectrum of Poly(bis(trifluoromethyl)norbornadiene) prepared *via*  $\text{RuCl}_3$  initiation

also shows the use of distortionless enhancement by polarization transfer (DEPT) in confirming the assignment of peaks. The bottom trace shows the normal broad band decoupled spectrum; the middle trace shows only the methine carbon signals; and the upper trace shows the methine carbons as positive peaks, the methylene carbons as negative peaks, and the quaternary carbon signals disappear in both DEPT spectra. At low field the resonances attributed to carbons 5 and 6 are distinguished from those due to carbon 4, since the quaternary carbon signals disappear in the DEPT spectrum, whereas the vinylic carbons appear as positive peaks. Carbon 6, which is directly bonded to three fluorine atoms, is easily identified as the quartet centred at 121.4 ppm ( $^1J_{C-F}=273\text{Hz}$ ). Carbon 5, which is  $\alpha$  to the  $\text{CF}_3$  group is shifted downfield, and identified as the broad unresolved peak at 139.3 ppm. The two remaining peaks in this region are the vinylic carbon signals. The weaker intensity peak appears to be resolved into two signals. This "splitting" could be assigned to m/r effects or vinylene sequence effects. The  $\sigma_C$  value calculated from these signals is 0.36. For a range of substituted polynorbornenes it is observed that  $\alpha$ -*cis* carbons appear 5 ppm upfield from  $\alpha$ -*trans* carbons, as in simple alkenes. The allylic carbons are therefore assigned as shown in Figure 3.3, giving a  $\sigma_C$  value of 0.36. The methylene carbon is centrally disposed between two double bonds, so that the tc and ct environments for this carbon are equivalent. The signals are assigned to the cc, ct $\equiv$ tc and tt environments, from low to high field, on the basis that the polymer has a high *trans* vinylene content. From these signals the value of  $\sigma_C$  is 0.34. Hence, the values of  $\sigma_C$  are intern-

ally consistent. In this assignment the line order for the allylic and methylene carbon signals parallels that found in poly(norbornene), although the line order for the vinylic carbon resonance is reversed.

(b) Catalysts Effecting the polymerization of (I)

Monomer (I) was subjected to a range of metathesis catalysts. The results from a selection of these polymerizations are given in Table 3.1

TABLE 3.1 Polymerization of 2,3-bis(trifluoromethyl)norbornadiene

Expt. No.	Monomer (mmole)	Catalyst (mmole)	Cocatalyst (mmole)	Solvent <sup>a</sup> (mls)	Temp <sup>b</sup> (°C)	Time (hrs)	Yield <sup>c</sup> (%)
1	5.58	MoCl <sub>5</sub> (0.028)	Me <sub>4</sub> Sn (0.056)	C, (2.2)	30	2 mins	87 <sup>d</sup>
2	27.19	WCl <sub>6</sub> (0.136)	Me <sub>4</sub> Sn (0.272)	C, (7.0)	25	2 mins	90
3	4.19	RuCl <sub>3</sub> (0.024)	-	CE, (0.5)	50	36	21
4	8.57	RuCl <sub>3</sub> (0.048)	Me <sub>4</sub> Sn (0.096)	CE, (1.5)	40	2.5	74
5	7.85	OsCl <sub>3</sub> (0.039)	-	CE, (1.6)	60	48	0
6	14.56	ReCl <sub>5</sub> (0.073)	-	C, (2.6)	60	72	0
7	9.80	IrCl <sub>3</sub> (0.017)	-	CE, (0.4)	40	48	0

- a. C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.
- b. Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.
- c. After reprecipitation and drying under vacuum for at least 24 hours.
- d. Chain transfer agent, trans-4-octene, added to reduce molecular weight.

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Experiments 5,6 and 7 were repeated several times, but in all cases no polymer was formed.

The <sup>13</sup>C n.m.r. spectra of the polymers produced in

experiments 1,2,3 and 4 were obtained; the  $\sigma_c$  values calculated for each sample are tabulated in Table 3.2 and the  $^{13}\text{C}$  n.m.r. shifts and assignments are shown in Table 3.3.

TABLE 3.2 *Cis* vinylene content ( $\sigma_c$ ) for samples of poly(bis-(trifluoromethyl)norbornadiene)

Expt. No.	Catalyst	$\sigma_c$			Average
		From vinylene carbon signals	From allylic carbon signals	From methylene carbon signals	
1	$\text{MoCl}_5/\text{Me}_4\text{Sn}$	0.13	0.15	0.13	0.14
2	$\text{WCl}_6/\text{Me}_4\text{Sn}$	0.47	0.47	0.45	0.46
3	$\text{RuCl}_3$	0.29	0.29	0.26	0.28
4	$\text{RuCl}_3/\text{Me}_4\text{Sn}$	0.36	0.36	0.34	0.35

TABLE 3.3  $^{13}\text{C}$  N.m.r. shifts and assignments of poly(2,3-bis-(trifluoromethyl)norbornadiene) prepared *via* different initiators, recorded at 90.56MHz, TMS internal ref.

Shift (ppm)				Assignment
$\text{MoCl}_5/\text{Me}_4\text{Sn}$	$\text{WCl}_6/\text{Me}_4\text{Sn}$	$\text{RuCl}_3$	$\text{RuCl}_3/\text{Me}_4\text{Sn}$	
139.39	139.30	139.36	139.36	C5
132.93	133.20	132.80	132.72	C4, t
131.50	131.70	131.40	131.47	C4, c
		131.23	131.32	C4, c
121.47, q, $^1J_{\text{C-F}}=274\text{Hz}$	122.0, q, $^1J_{\text{C-F}}=273\text{Hz}$	121.36, q, $^1J_{\text{C-F}}=273\text{Hz}$	121.42, q, $^1J_{\text{C-F}}=273\text{Hz}$	C6
49.22	49.55	49.18	49.22	C2, t
44.14	44.48	44.07	44.16	C2, c
38.00	38.30	37.96	37.91	C3, cc
37.45	37.80	37.37	37.44	C3, ct $\equiv$ tc
36.65	36.80	36.54	36.56	C3, tt

*Cis* and *trans* environments of the vinyl carbons are the only features of microstructure which are clearly resolved in the spectra. The C4 resonance shows some fine structure which may be due to tacticity, or vinylene sequence effects, but it is impossible to determine which on the basis of the available data.

The results of the successful polymerizations are not exceptional; typically molybdenum based catalysts give polymers with a range of  $\sigma_c$  values, and Ru based catalysts give polymers with a high *trans* vinylene content.<sup>8</sup>

The reason for the failure to achieve a successful polymerization of (I) using Os, Ir and Re based catalysts is not immediately apparent. A rationale for the failure of  $\text{ReCl}_5$  catalyst to initiate the polymerization of (I) may be advanced on the basis of the different microstructures available for the polymer, which are shown in Figure 3.4. A *cis* isotactic stereochemistry is probably unfavourable due to the steric crowding of the  $\text{CF}_3$  substituents. Indeed, attempts to assemble a Courtaulds space filling molecular model with this stereochemistry proved extremely difficult. Similarly, a *cis* syndiotactic assembly is sterically crowded, although this is not obvious from a two dimensional drawing. However, on building a space filling model with this tacticity it is obvious that the methylene group and the  $\text{CF}_3$  substituent from a very crowded environment, making a *cis* syndiotactic structure very unfavourable. By contrast, the *trans* syndiotactic and isotactic geometries are considerably less crowded.

The polymer with the highest content of *cis* double bonds was formed *via*  $\text{WCl}_6$  initiation, giving a  $\sigma_c$  value of 0.46.

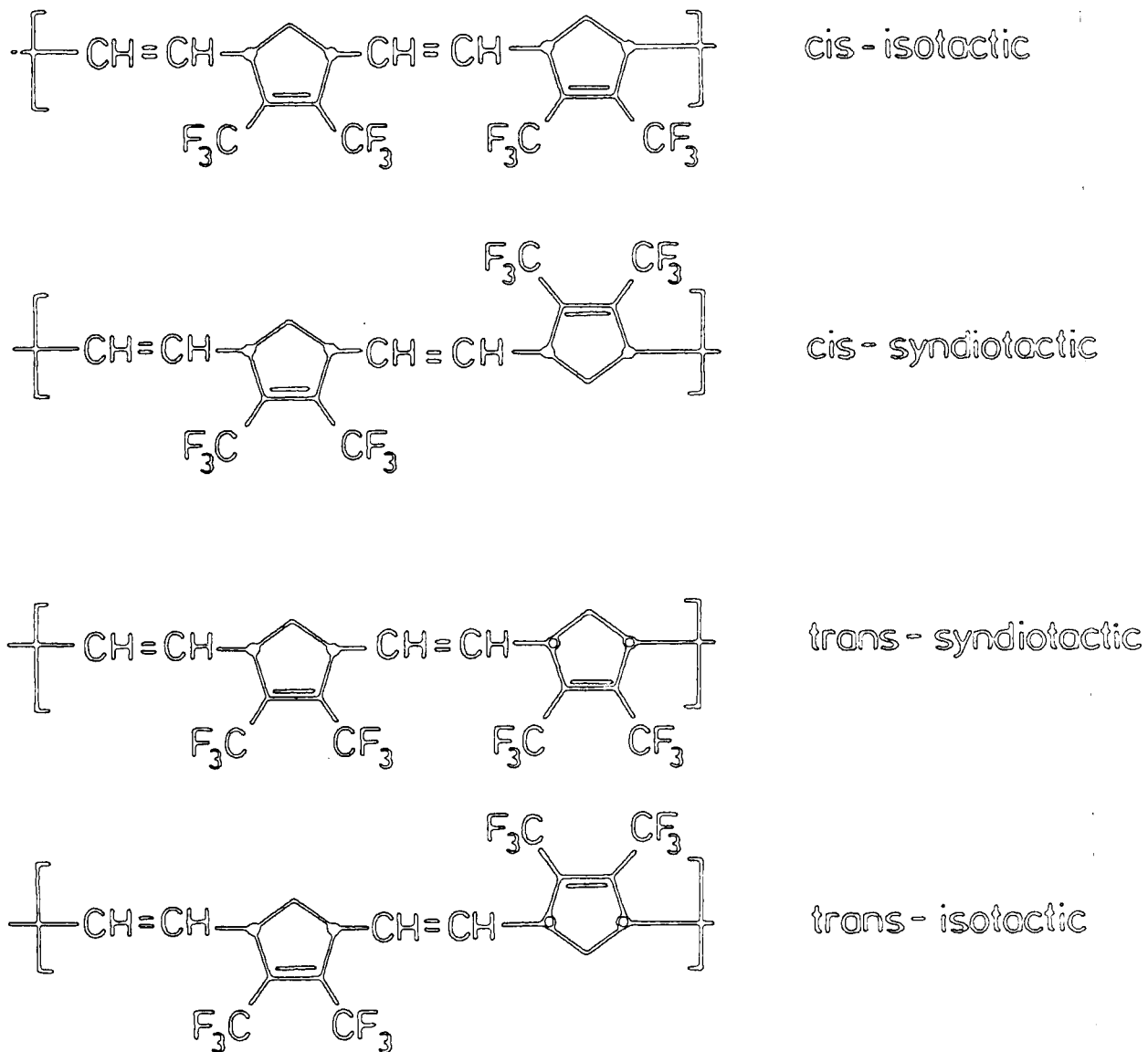


FIGURE 3.4 Assembly modes for poly(bis(trifluoromethyl)norbornadiene)

The methylene carbon resonance gives information on the *cis/trans* double bond distribution along the chain from the relative integral of the cc, ct≡tc, and tt resonances. In the spectrum of the tungsten derived polymer the cc peak has approximately half the intensity of the ct≡tc signal, which is slightly more intense than the tt peak. Hence, *cis-cis* junctions are not very prevalent, and although it is not proved by the data, it is possible that repeated formation of *cis* blocks does not occur. Hence, as rhenium pentachloride is known to produce polymers with a high *cis* vinylene content, and it appears that *cis* blocks of polymer I are unfavourable, we have a rationale for the failure of this catalyst to polymerize monomer (I).

In one case, however, an anomalous result was obtained. Polymerization of (I) using  $\text{ReCl}_5$  catalyst was attempted. After 48 hours at  $\approx 50^\circ\text{C}$  the monomer had not polymerized. The monomer and solvent from the polymerization were recovered by vacuum transfer, and the solution obtained was then polymerized using  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  as the initiator. A  $^{13}\text{C}$  n.m.r. of the polymer formed gave  $\sigma_{\text{C}}$  values of 0.79 for the vinylene carbons, 0.80 for the allylic carbons and 0.76 for the methylene carbons; 66% of the methylene carbon peak was assigned to the cc environment. This unusual result could not be repeated on a second attempt, and was not pursued further due to the limited access to the high field n.m.r. instrument required for product analysis. Nevertheless, this result indicates that a high *cis* polymer can be formed from monomer (I), but unfortunately the experimental conditions required to achieve this result are not well defined. It may be that during the initial attempted polymerization of monomer (I) using  $\text{ReCl}_5$ ,



low molecular weight *cis* oligomers were formed; these were then vacuum transferred and on subsequent polymerization with a more active catalyst system, the preformed geometry of the oligomers forces coordination of the metal centre in such a way that *cis* double bonds are formed. Alternatively, a rhenium organometallic complex of (I) may have been vacuum transferred, which subsequently initiated polymerization to give *cis* double-bonds.

It is possible that steric restrictions in the transition state giving rise to *cis* double bonds is the important factor. During the formation of *cis* vinylenes it has been postulated that the newly formed double bond remains within the coordination sphere of the metal as the next monomer approaches (see Section 1.9c), as depicted in Figure 3.5.

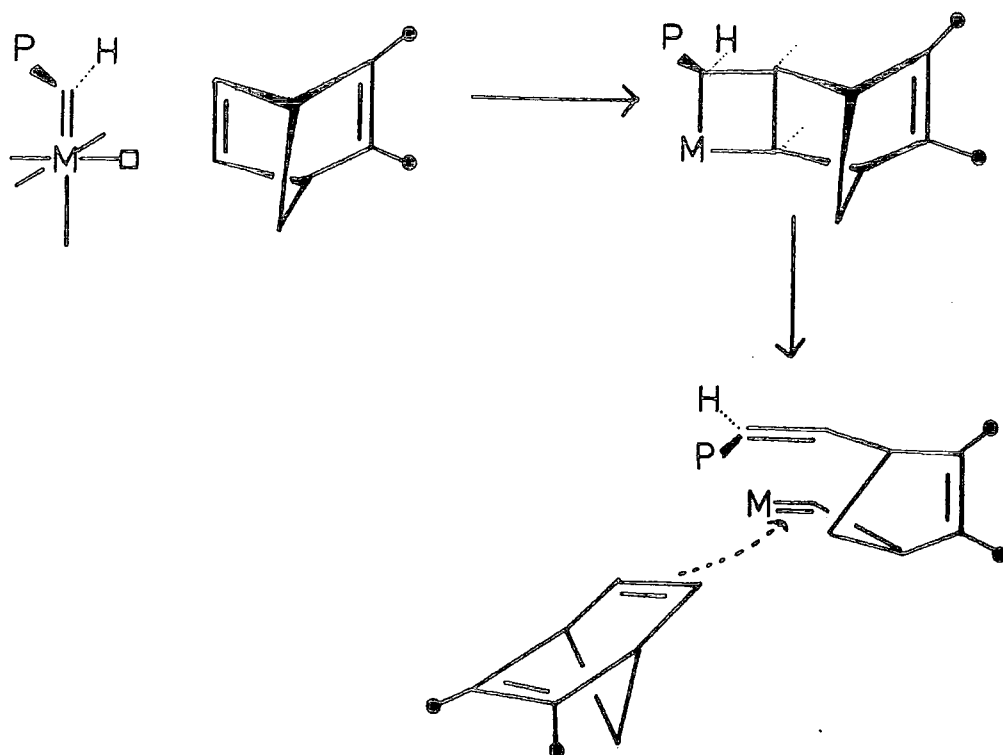


FIGURE 3.5 Formation of *cis* vinylenes



It is evident that the  $\text{CF}_3$  substituents in the initial metallocyclobutane are far removed from the metal centre, and unlikely to cause any steric hindrance. However, as the next monomer approaches there may be some steric repulsion between the methylene group of the cyclopentene ring adjacent to the metal carbene, and the  $\text{CF}_3$  substituents of the incoming monomer. When 2-trifluoromethyl norbornadiene is polymerized to give a high *cis* polymer, HH units are observed, and therefore this type of hindrance, even if present, does not prevent formation of polymer. Hence, it seems more likely that steric restrictions in the chain itself usually prevents formation of high polymer.

A rationalization of the failure of Os and Ir based catalysts to effect the polymerization of (I) can also be constructed. Since these catalysts typically give polymers with a high *trans* vinylene content, and it has been postulated that *trans* geometries are relatively unhindered, it might be expected that these polymerizations would occur with ease. The initial step in the polymerization mechanism involves coordination to the active metal centre, and it seems that (I) is a good enough donor for this process.

However, it is possible that the metal centres complex to the monomer, which may act as a bidentate ligand. This type of behaviour has been observed for the polymerization of endo-dicyclopentadiene using ruthenium trichloride as catalyst<sup>11</sup> (see Section 1.4). The increased steric bulk at the catalyst centre, as a result of complexation, forces the monomer to approach so that a *cis* double bond is formed. However, in the case of monomer (I) it has been postulated that successive formation of *cis* double bonds is not favourable

and hence Ir and Os chlorides are ineffective catalysts. Nevertheless, the reason why this effect does not inhibit the polymerization of (I) using  $\text{RuCl}_3$  remains unanswered. The questions raised by these observations merit attention, but are clearly experimentally difficult to investigate and would require considerable instrument time, which was not available to the author.

(c) Polymerization of (I) using  $\text{MoCl}_5/\text{Me}_4\text{Sn}$

The results tabulated in Table 3.2 indicate that the  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  catalyst system produces the polymer with the highest degree of order. A more detailed analysis of this polymerization was carried out and the polymer microstructure examined as a function of temperature.

Monomer (I) was polymerized using  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  as catalyst in the range  $-20$  to  $100^\circ\text{C}$ . The details of the experiments are recorded in Table 3.4.

TABLE 3.4 Polymerization of (I) using  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  catalyst at different temperatures

Expt. No.	Temperature <sup>a</sup> ( $^\circ\text{C}$ )	Monomer (mmoles)	Catalyst (mmole)	Cocatalyst (mmole)	Trans-4 <sup>b</sup> octene (mmole)	Solvent (mls)	Time (hours)	Yield (%)
1	-20	74.69	0.037	0.074	-	2	48	c
2	0	18.64	0.093	0.018	-	0.5	24	67 <sup>c</sup>
3	20	7.02	0.035	0.070	-	2.2	1 min	83 <sup>c</sup>
4	30	6.28	0.031	0.062	0.15	2.2	2 min	64
5	40	7.39	0.039	0.078	0.32	2.2	5 min	85
6	60	6.32	0.032	0.064	0.15	2.1	1 min	79
7	80	10.17	0.050	0.100	0.51	5.2	2 min	85
8	98	3.38	0.019	0.038	0.15	2.1	2 min	91

a. Temperature measured by inserting thermometer into stirred reaction solution.

b. trans-4-octene added to reduce the molecular weight of the polymer.

c. insoluble.

The temperature of the reaction mixture was monitored and the catalyst solution added at a rate which maintained the required temperature. The polymerization reaction is notably exothermic, and the catalyst solution was added over several minutes to the stirred reaction mixture to prevent any detectable increase in temperature. The polymerization was terminated by the addition of a small amount ( $\sim 1\text{cm}^3$ ) of methanol, and the polymer precipitated by pouring into a large excess of hexane. The polymer was recovered, dried, dissolved in acetone, and purified by successive reprecipitation into hexane. Attempts to produce a soluble polymer from experiments 1,2 and 3 by limiting the molecular weight *via* addition of *trans*-4-octene were not successful; addition of small quantities of the chain transfer agent had little effect on the molecular weight and served only to reduce the yield of polymer.

$^{13}\text{C}$  N.m.r. spectra of the soluble samples were obtained and the  $\sigma_{\text{C}}$  values calculated for each. Figure 3.6 shows a graph of the percentage *trans* vinylene content plotted against the polymerization temperature. The straight line through the points represents a least squares fit. There is no theoretical justification for a linear relationship, but nevertheless the graph shows there is only a small temperature dependence of the *trans* vinylene content over the range studied. As the temperature is decreased the *cis* vinylene content is increased. This type of effect is observed for the polymerization of cyclopentene initiated by  $\text{WCl}_6/(\text{CH}_2=\text{CHCH}_2)_4\text{Si}^{156}$ . At  $20^\circ\text{C}$  the polymer has a  $\sigma_{\text{C}}$  value of 0.4, which rapidly increases as the temperature is decreased, reaching a value of

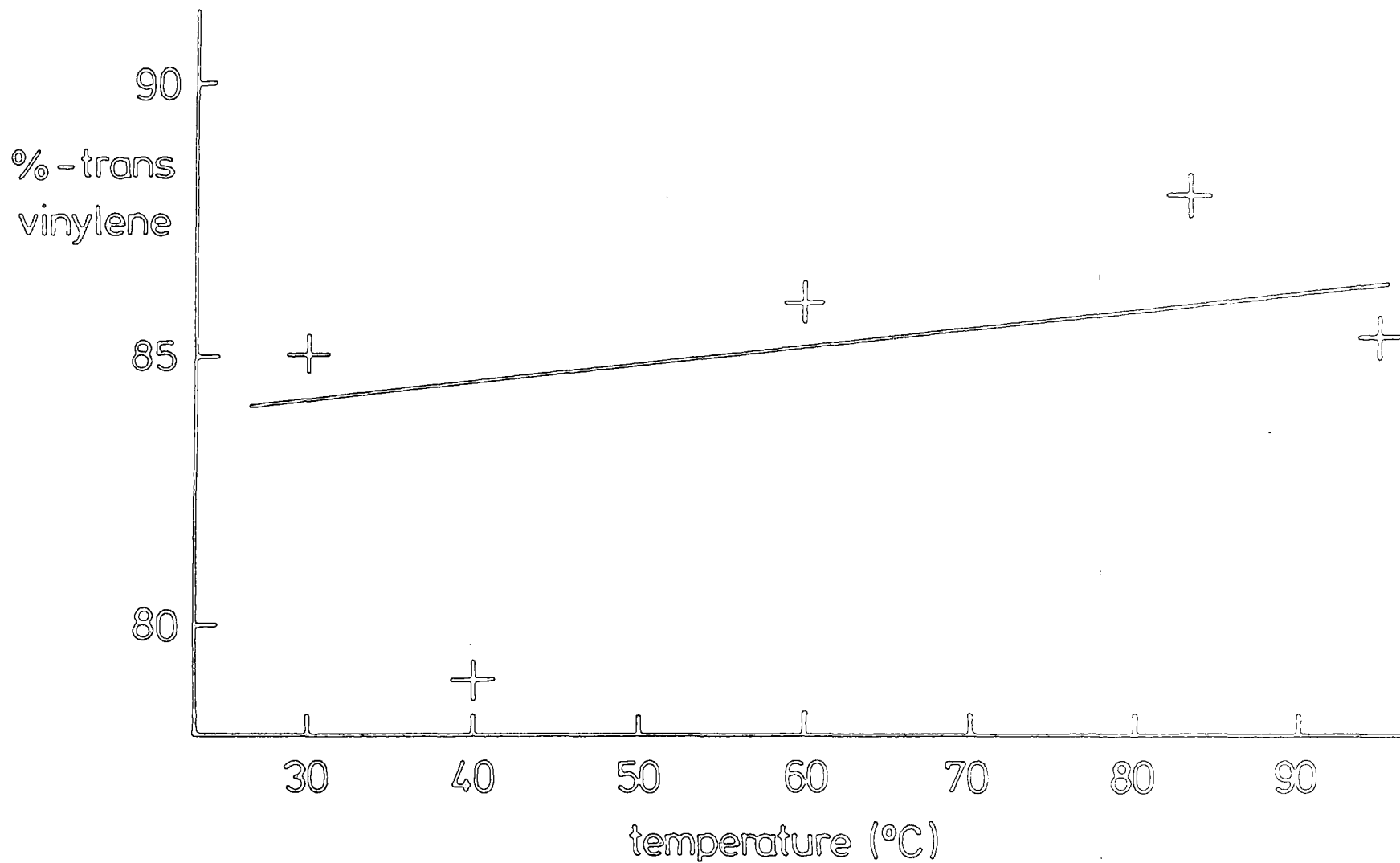


FIGURE 3.6 Graph of the *trans* vinylene content of polymers of (I) prepared via  $\text{McCl}_5/\text{Me}_4\text{Sn}$  initiation, as a function of the polymerization temperature

$\approx 0.98$  at  $-20^{\circ}\text{C}$ . Had the samples of polymers of (I) prepared at low temperature been soluble, then a similar effect may have been observed.

(d) Infrared spectra of Polymers of (I)

Infrared spectra of thin films of poly(bis(trifluoromethyl)norbornadiene) prepared *via* molybdenum and tungsten based catalyst were obtained on a Nicolet 60SX Interferometer. The polymers derived from these catalysts show the greatest difference in *cis* vinylene content, and are therefore the most likely to show differences in their infrared spectra. Three regions of the spectra are of interest; the C-H stretching region above  $3000\text{ cm}^{-1}$  where the *trans* absorption occurs at a higher frequency than the *cis* absorption; the C=C stretching region around  $1660\text{ cm}^{-1}$ ; and the C-H out of plane bending region around  $965\text{ cm}^{-1}$  for *trans* vinylenes and  $730\text{ cm}^{-1}$  for *cis* vinylenes.

Figure 3.7 shows the C-H stretching region and it is clear that in the molybdenum derived sample the band at  $3043\text{ cm}^{-1}$  is more intense than the band at  $3022\text{ cm}^{-1}$ , indicating a higher *trans* vinylene content in this polymer. This observation is in agreement with the results obtained from the  $^{13}\text{C}$  n.m.r. spectra.

The C=C stretching region of the infrared spectra is shown in Figure 3.8. This region is dominated by the strong  $-(\text{CF}_3)-\text{C}=\text{C}-(\text{CF}_3)-$  band at  $1682\text{ cm}^{-1}$ . The shoulder on the major peak is probably the  $-\text{CH}=\text{CH}-$  stretching absorption which appears stronger in the Mo based sample. This mode would be expected to be strongest for the *cis* vinylene and this observation contradicts the earlier assignment. It would,

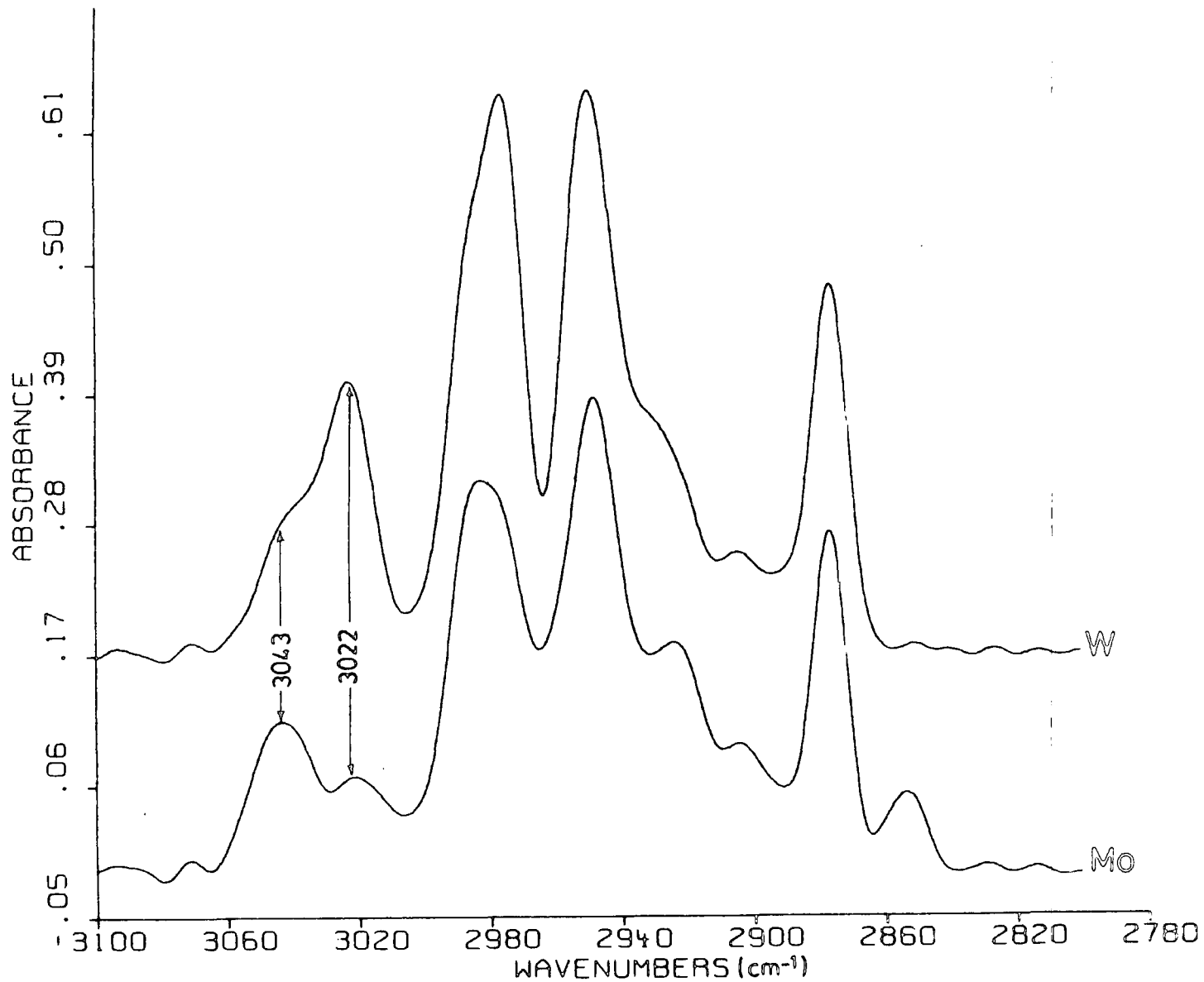


FIGURE 3.7 C-H stretching region of the infrared spectra of Poly(bis(trifluoromethyl)norbornadiene). Prepared via Mo and W initiation

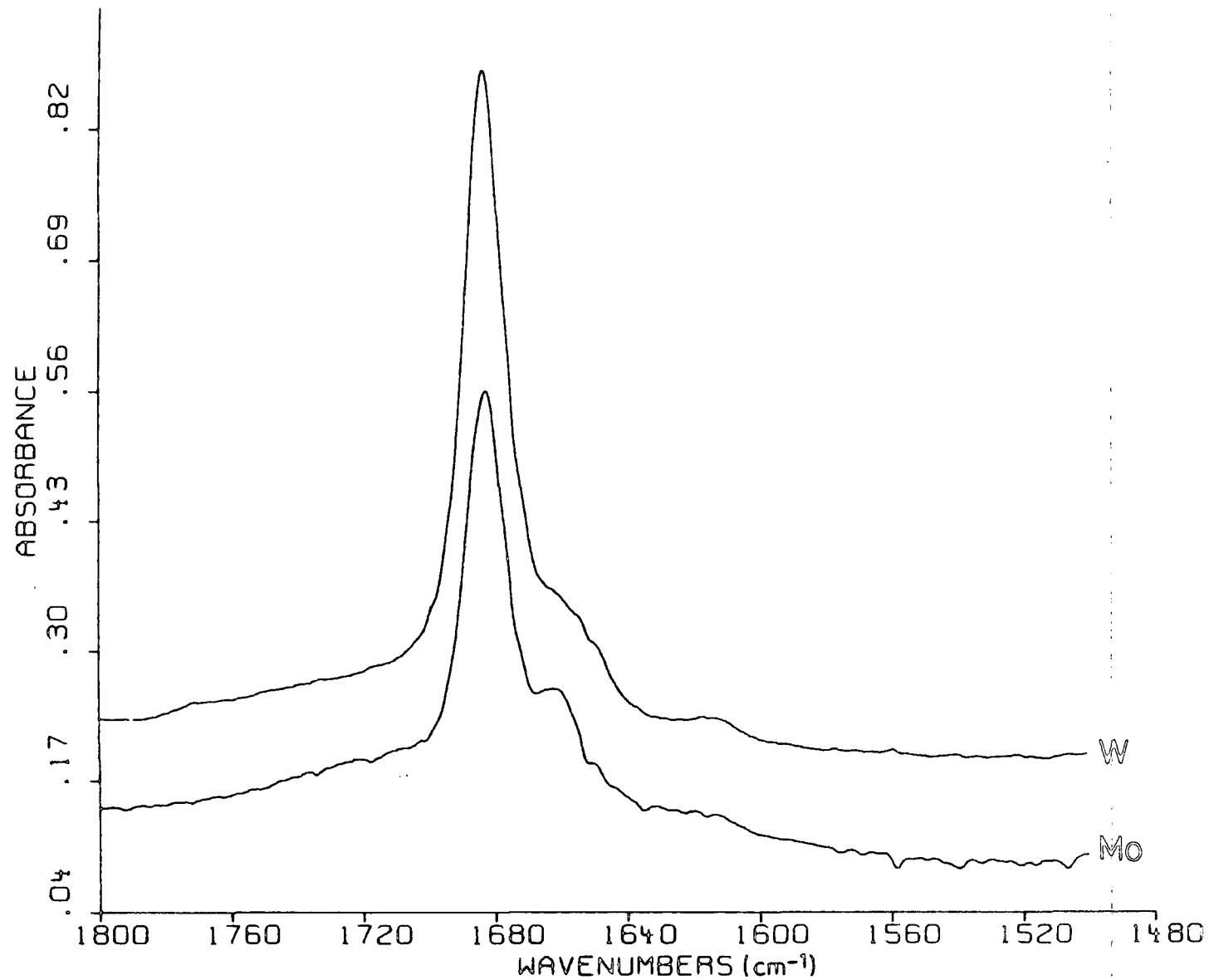


FIGURE 3.8 C=C stretching region of the infrared spectra of polymers of bis(trifluoromethyl) norbornadiene prepared via Mo and W initiation



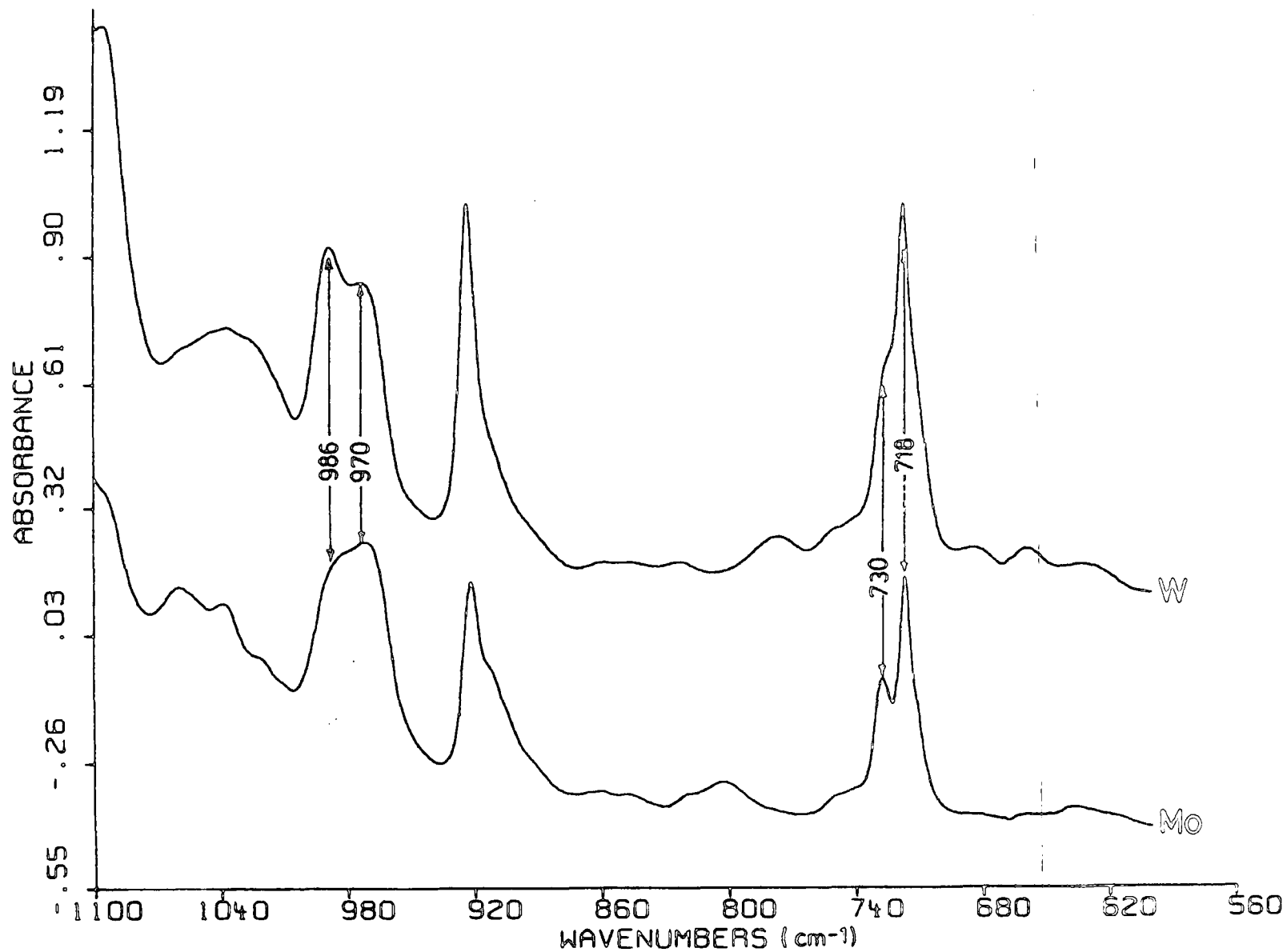


FIGURE 3.9 C-H Out of plane bends of samples of poly(bis(trifluoromethyl)norbornadiene) prepared via Mo and W initiation

however, be unwise to attach too much weight to this observation due to the weak intensity of the peaks involved and the dominance of the  $-\text{CF}_3-\text{C}=\text{C}=\text{CF}_3-$  absorption.

The vinylene C-H out of plane bending absorptions occur in the region depicted in Figure 3.9. This part of the spectrum is complicated since two pairs of bands are observed in the *trans* region at 986 and 970  $\text{cm}^{-1}$ , and in the *cis* region at 730 and 718  $\text{cm}^{-1}$ . It is possible that both sets of absorptions are out of plane bends, in which case the  $\text{MoCl}_5$  derived polymer contains more *trans* vinylenes than the  $\text{WCl}_6$  derived sample. Alternatively, if only one of the bands from each pair arises from an out of plane bend, and the band at 730  $\text{cm}^{-1}$  is assigned to the *cis*, and at 970  $\text{cm}^{-1}$  to the *trans* unit, then again the molybdenum derived sample has the greater *trans* vinylene content.

Thus, overall the infrared spectra of the samples confirm the assignments obtained from the  $^{13}\text{C}$  n.m.r. spectra.

### 3.5 Polymerization of 2-trifluoromethylnorbornadiene (II)

#### (a) Catalysts Effecting the Polymerization of (II)

2-Trifluoromethylnorbornadiene was subjected to a range of metathesis catalysts and the results of the reactions are recorded in Table 3.5. The polymerizations carried out in collaboration with Mr. P.C. Taylor are marked with an asterisk (\*).

TABLE 3.5 Polymerization of 2-trifluoromethylnorbornadiene

Expt. No.	Monomer (mmole)	Catalyst (mmole)	Cocatalyst (mmole)	Solvent <sup>a</sup> (mls)	Temp <sup>b</sup> (°C)	Time (hrs)	Yield <sup>c</sup> (%)
1*	9.75	MoCl <sub>5</sub> (0.049)	Me <sub>4</sub> Sn (0.098)	C (7)	RT	5 mins	50
2*	11.87	WCl <sub>6</sub> (0.059)	Me <sub>4</sub> Sn (0.118)	C (4.6)	RT	5 mins	~90
3	8.31	RuCl <sub>3</sub> (0.041)	-	CE (0.2)	40	65	5
4*	7.50	OsCl <sub>3</sub> (0.037)	-	CE (0.3)	40	2.5	25
5	12.60	IrCl <sub>3</sub> (0.063)	CF <sub>3</sub> COOH (0.313)	CE (1.5)	40	48	25
6	8.50	ReCl <sub>5</sub> (0.042)	-	C (0.3)	60	48	7

- a. C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.
- b. Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.
- c. After reprecipitation and drying under vacuum for at least 24 hours.

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The results indicate that it is possible to polymerize 2-trifluoromethylnorbornadiene (monomer II) with a wider range of catalysts than 2,3-bis(trifluoromethyl)norbornadiene (monomer I); monomer (I) could not be polymerized in any of several attempts using Ir, Os or Re based catalysts. This implies that replacing one of the trifluoromethyl groups in (I) by a hydrogen has the effect of increasing the monomers susceptibility to polymerization. It is possible that the decreased steric bulk in the chain of the polymer derived from monomer (II) is responsible for this effect. The increased space may allow HH environments to be formed more readily, in which rotation of the bonds around the allylic carbons gives a conformation where repulsion between the CF<sub>3</sub> groups is minimised. Ru, Os and Ir based catalysts all initiate the polymerization of monomer (II).

(b) Infrared spectra of polymers of (II)

The infrared of the polymers of 2-trifluoromethyl-norbornadiene were obtained, and it was found that the spectra of the polymers derived from experiments 1-5 (Table 3.5) were virtually superimposable and different from that of the polymer obtained *via* rhenium pentachloride initiation (experiment 6). Figure 3.10 shows the spectra of the polymers obtained from  $\text{OsCl}_3$  and  $\text{ReCl}_5$  catalysts.

The spectra are dominated by the intense absorptions between  $1350$  and  $1100\text{ cm}^{-1}$  associated with the trifluoromethyl group. The C-H and C=C stretching absorptions in the  $3000$  and  $1650\text{ cm}^{-1}$  regions respectively are consistent with the expected structure, but no other structurally useful information could be derived from them. However, the vinylic C-H out of plane bending modes are well resolved and do not overlap with other absorbances. The polymer obtained *via*  $\text{OsCl}_3$  initiation (shown in Figure 3.10b) shows bands at  $970\text{ cm}^{-1}$  (*trans*) and  $730\text{ cm}^{-1}$  (*cis*) indicating both *cis* and *trans* vinylenes are present. In contrast, the  $\text{ReCl}_5$  derived polymer (shown in Figure 3.10a) has a relatively strong band at  $730\text{ cm}^{-1}$  and a very weak absorption at  $970\text{ cm}^{-1}$ , indicating a high *cis* vinylene content. Since the polymers derived from Ru, Ir, Mo and W halides gave similar infrared spectra to the  $\text{OsCl}_3$  derived polymer, it can be concluded that these polymers all contain a mixture of *cis* and *trans* vinylenes.

(c)  $^{13}\text{C}$  N.m.r. spectra of polymers of (II)

There was some variation in the quality and detail of the  $^{13}\text{C}$  n.m.r. spectra of polymers of (II) but they all gave spectra with the same overall appearance, with the exception

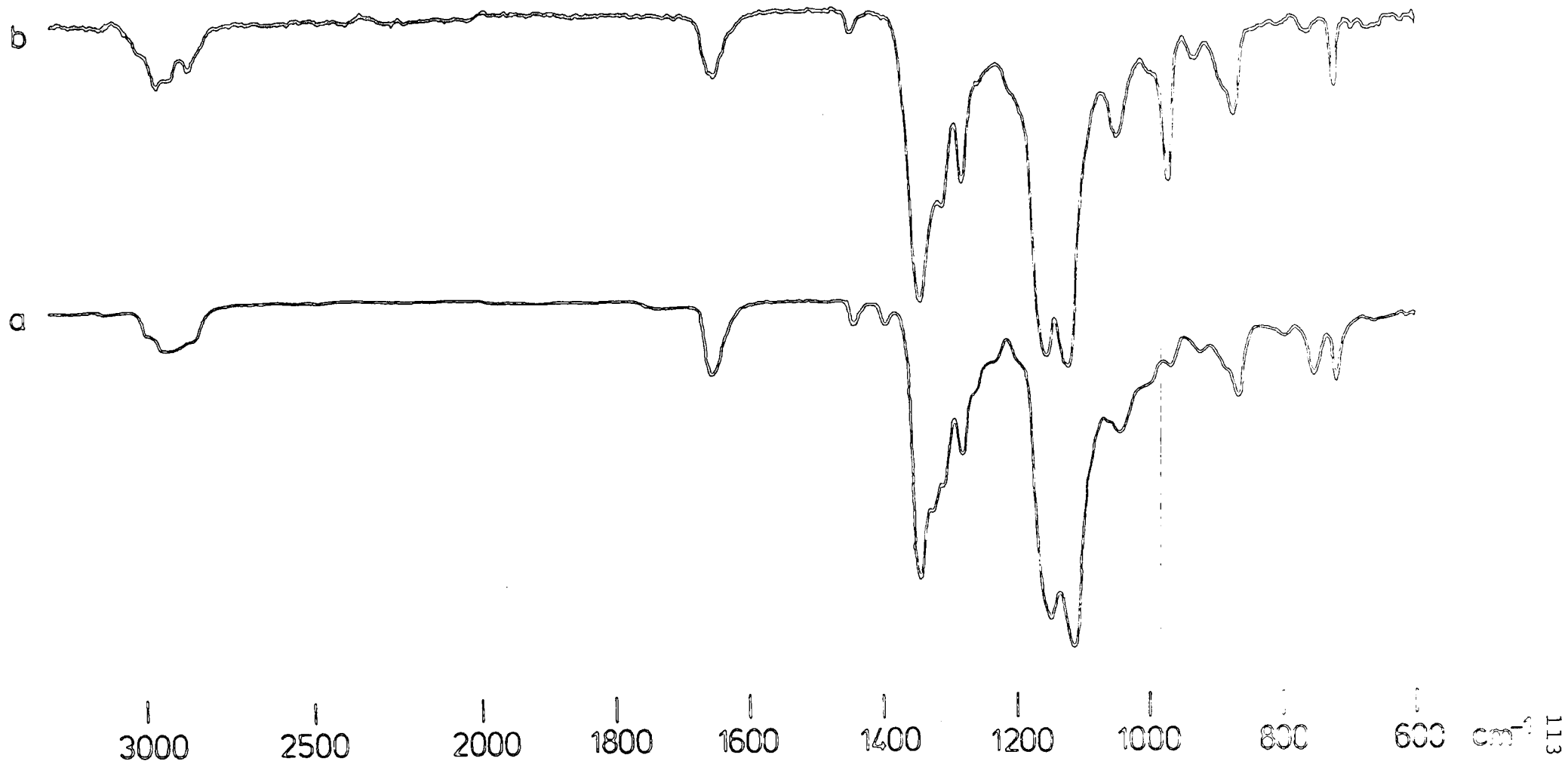
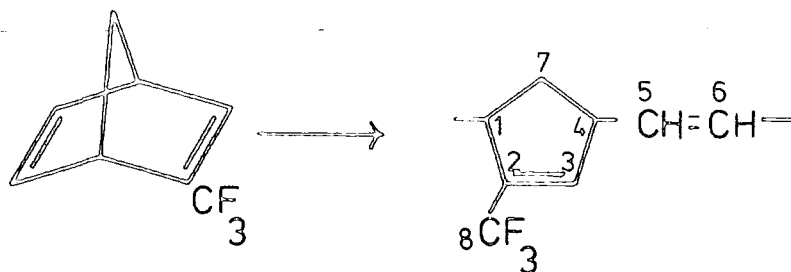


FIGURE 3.10 Infrared spectra of samples of poly(2-trifluoromethylnorbornadiene) prepared via  $\text{CsCl}_3$  initiation (b) and  $\text{ReCl}_5$  initiation (a)

of the polymer prepared *via*  $\text{ReCl}_5$  initiation. The spectra recorded for polymers obtained *via*  $\text{OsCl}_3$  and  $\text{ReCl}_5$  catalysis are reproduced in Figures 3.11 and 3.12 respectively. The spectra are consistent with the polymers being the products of ring opening. The numbering system used when assigning the spectra is shown below.



The spectrum of the polymer derived from  $\text{OsCl}_3$  initiation is considered to illustrate the assignment of peaks. The DEPT spectra allow the methylene, methine, quaternary and vinylene carbon signals to be distinguished. The poorly resolved quartet at 135.9 ppm ( $^2J_{\text{C-F}}=30\text{Hz}$ ) is assigned to C2, and the quartet centred at 123.2 ppm ( $^1J_{\text{C-F}}=27\text{Hz}$ ) attributed to C8. The resonance at lowest field, centred at 140.4 ppm, is associated with C3, and its broadness is probably a consequence of the fact that it represents the sum of signals from several non-equivalent environments. The multiplet located between 133.3 and 131.7 ppm is assigned to the different environments of the vinylene carbons, C5 and C6. The multiplicity of these signals indicates that there are a number of different environments for these carbons.

In the high field region of the spectrum the methylene carbon resonance is easily identified, with the aid of the DEPT spectrum, as the multiplet centred at 39.3 ppm. The resonance

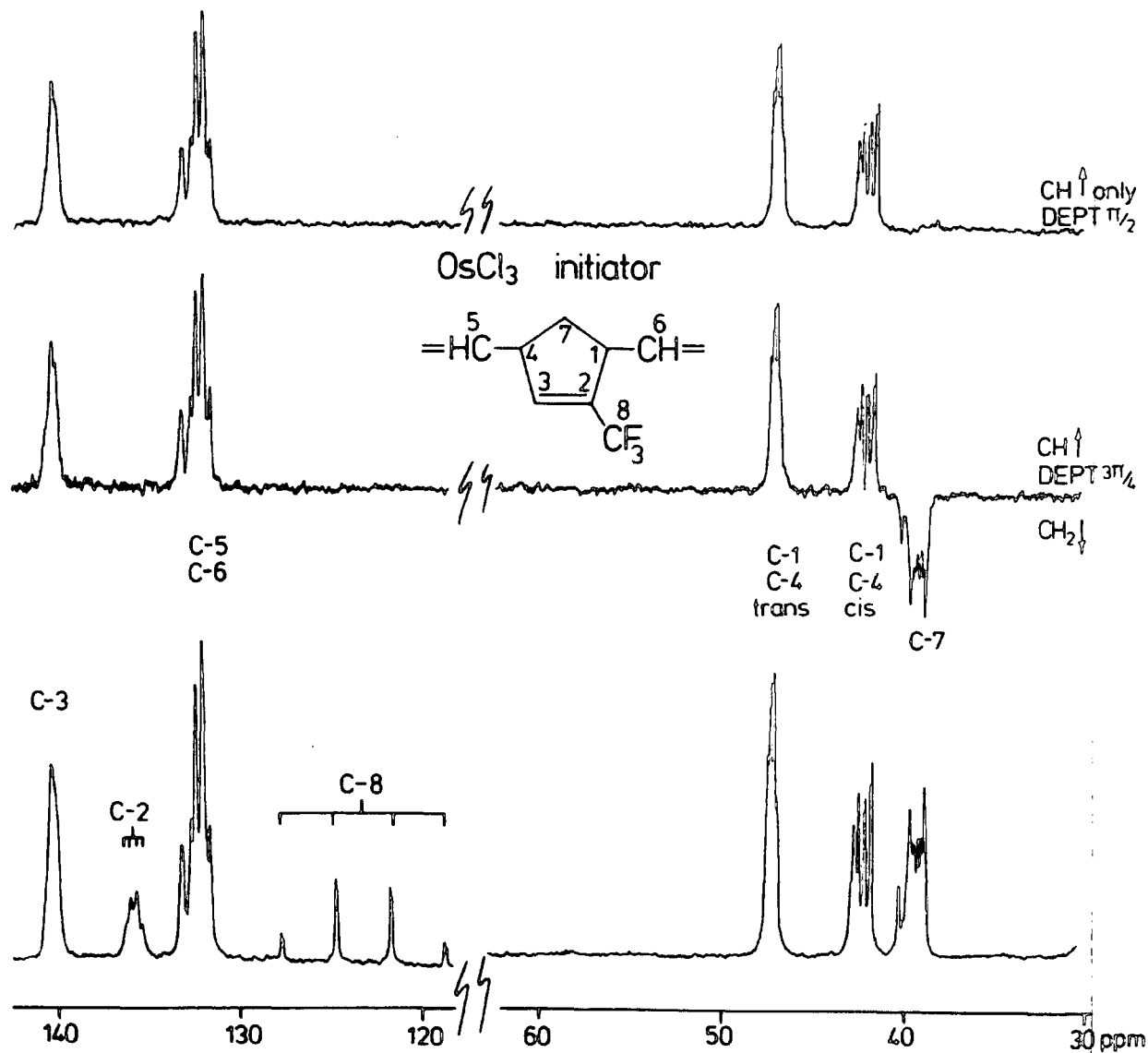


FIGURE 3.11 <sup>13</sup>C N.m.r. spectrum of poly(2-trifluoromethylnorbornadiene) prepared *via* OsCl<sub>3</sub> initiation

located between 41.8 and 42.9 ppm can be confidently assigned to the allylic carbons adjacent to *cis* vinylenes, and that between 47.2 and 47.5 ppm attributed to allylic carbons adjacent to *trans* vinylenes. The difference in shift between the *cis* and *trans* allylic carbon resonances is 5 ppm, as anticipated. The multiplicity of the signals gives rise to a very complicated spectrum, which has so far defied a detailed interpretation. The spectra of the polymers derived from W, Mo, Ru and Ir all show a varying degree of resolution and it can be concluded that all have both *cis* and *trans* vinylenes in the polymer chain backbone. In contrast, the spectrum of the polymer derived *via* Re initiation is very simple. The value of  $\sigma_c$  for each polymer, calculated from the integral of the allylic carbon resonances, are recorded in Table 3.6.

TABLE 3.6 *Cis* vinylene content ( $\sigma_c$ ) for samples of poly-(2-trifluoromethylnorbornadiene)

Catalyst	$\sigma_c$ (calculated from allylic carbon signals)
MoCl <sub>5</sub> /Me <sub>4</sub> Sn	0.30
WCl <sub>6</sub> /Me <sub>4</sub> Sn	0.48
OsCl <sub>3</sub>	0.45
RuCl <sub>3</sub>	0.44
IrCl <sub>3</sub>	0.46
ReCl <sub>5</sub>	0.86

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If the  $\sigma_c$  values for poly(2-trifluoromethylnorbornadiene) are compared with those of poly(2,3,-bis(trifluoromethyl)-norbornadiene) (Table 3.2) it is apparent that the more readily



polymerized monomer (II) also displays a lower selectivity in its polymerization with a variety of catalysts. Thus, the very active catalyst system  $WCl_6/Me_4Sn$  does not discriminate between (I) and (II) giving equal proportions of *cis* and *trans* vinylenes, whereas Mo and Ru based catalysts both give a higher selectivity with (I) than with (II), and the Os, Ir and Re catalysts fail to polymerize (I) at all.

Generally, Os, Ru and Ir based catalysts give polymers with a high *trans* vinylene content. The poor selectivity observed in these polymerizations can be explained in terms of co-ordination of the metal centre with the monomer, as described previously. In the case of monomer (I) this type of interaction was postulated to prevent formation of polymer due to the necessity to form *cis* HH units. In monomer (II) it seems that *cis* HH junctions will be formed with greater ease. Alternatively, the *cis* units could be formed with an all HT structure, avoiding the requirement to form HH units. However, the complexity of the spectra make this possibility seem unlikely. The fact that the catalysts give polymers with both *cis* and *trans* double bonds suggests the chelation effect is not particularly important in these systems.

The  $^{13}C$  n.m.r. of the polymer derived from  $ReCl_5$  is shown in Figure 3.12, and the shifts and assignments tabulated in Table 3.7.

At low field the C8 and C2 resonances are easily identified with the aid of the DEPT spectrum. The C3 vinylene carbon resonance appears at lowest field and is considerably sharper than in the spectrum of the  $OsCl_3$  derived polymer, indicating an increased structural homogeneity. The carbon

ReCl<sub>5</sub> initiator

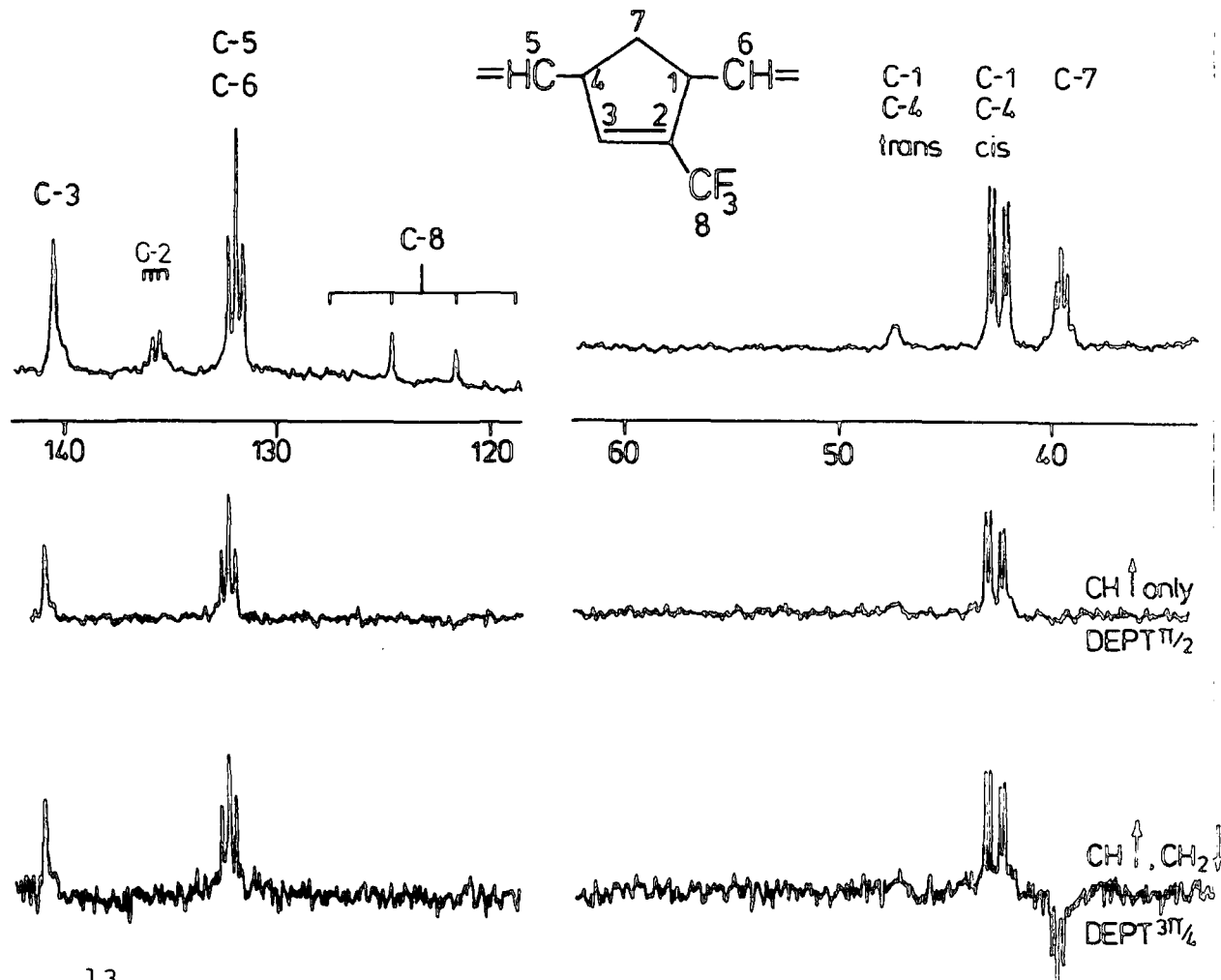


FIGURE 3.12 <sup>13</sup>C N.m.r. spectrum of poly(2-trifluoromethylnorbornadiene) prepared *via* ReCl<sub>5</sub> initiation

TABLE 3.7  $^{13}\text{C}$  N.m.r. shifts and assignments of poly(2-trifluoromethylnorbornadiene) obtained via  $\text{ReCl}_5$  initiation

Shift (ppm)	Assignment
140.71	C3 <i>cis</i>
135.85	C2 <i>cis</i>
132.48	)
132.13	) C5/6 <i>cis</i>
131.80	) HH, HT, TH and TT
124.74	C8
47.32	C1/4 <i>trans</i>
42.95	] C1 or C4 <i>cis</i>
42.70	
42.26	] C1 or C4 <i>cis</i>
42.04	
39.86	)
39.64	) C7 <i>cis</i>
39.33	)

signals C5 and C6 appear as 3 lines in the approximate ratio 1:2:1; the polymer has a high *cis* vinylene content and these lines are provisionally assigned to *cis* TH, TT, HH and HT environments, where the middle peaks represent coincidence of two environments.

At high field the resonance for the allylic carbons adjacent to *cis* double bonds consists of two sets of two signals at 42.95 and 42.26 ppm, and 42.70 and 42.04 ppm. This assignment is based on the fact that the total intensity of the C4 resonance must equal the intensity of the C1 signal; the higher field signal in each pair has a lower intensity

than the low field signal. The C'7 resonance appears as 3 lines in the approximate ratio 1:2:1; these signals are assigned to the HH, HT, TH and TT effects from adjacent rings, with the middle signal again representing chemical shift equivalence of two environments. It is possible that the observed resolution of carbon resonances could be attributed to m/r effects in an all HH/TT or all HT polymer. However, when resolution due to m/r effects has been observed previously<sup>67</sup> it was usually in the HH vinylene carbon environment. It seems unlikely that m/r resolution would be observed for all signals, and therefore it is highly probable that this high *cis* polymer has an approximately equal distribution of HH, HT, TH and TT assembly modes and with all m or all r dyads. It is, however, impossible to determine unambiguously which is the case on the basis of the available data. The fact that the HH and HT signals for C1, and the TT and TH signals for C4 have slightly different intensities suggest there may be a small degree of HH/TT or HT bias in the polymer

### 3.6 Polymerization of endo (III) and exo (IV) 5-trifluoromethylnorbornene

#### (a) Catalysts effecting the polymerization of (III) and (IV)

Exo and endo-5-trifluoromethylnorbornene were separated by preparative scale gas chromatography. Small quantities of each were obtained and hence, the monomers were not subjected to the full range of catalysts. All the polymerizations that were attempted were successful and the details of the experiments are recorded in Table 3.8.

TABLE 3.8 Polymerization of endo and exo-5-trifluoro-  
methylnorbornene

Expt. No.	Monomer (mmole)	Catalyst (mmole)	Cocatalyst (mmole)	Solvent <sup>a</sup> (cm <sup>3</sup> )	Temp <sup>b</sup> (°C)	Time (hrs)	Yield <sup>c</sup> (%)
A	Exo (9.63)	OsCl <sub>3</sub> (0.048)	none	CE (0.3)	40	12	38
B	Endo (1.23)	OsCl <sub>3</sub> (0.006)	none	CE (0.2)	40	5	30
C	Endo (7.22)	MoCl <sub>5</sub> (0.036)	Me <sub>4</sub> Sn (0.072)	C (0.2)	RT	2 min	65
D	Endo (6.75)	ReCl <sub>5</sub> (0.033)	none	CE (0.25)	40	2	10

- a. C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.
- b. Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.
- c. After reprecipitation and drying under vacuum for at least 24 hours.
- 

(b) Infrared Spectra

The C-H vinylene stretching region of the infrared spectra gives no useful information other than to confirm that the polymers are unsaturated. The region 1600-400 cm<sup>-1</sup> is depicted in Figure 3.13. It can be seen that the spectra of the polymers are all very similar except in the *cis* and *trans* out of plane bending regions. The spectrum of the polymer derived from OsCl<sub>3</sub> initiation of the exo isomer is shown in (A) and has a strong 970 cm<sup>-1</sup> absorption (*trans*) and no absorption at 730 cm<sup>-1</sup>, indicating the polymer has a high *trans* vinylene content. The infrared spectra of the OsCl<sub>3</sub> and MoCl<sub>5</sub> derived polymers (shown in B and C respectively) indicate that these polymers have a high *trans* vinylene content, but also show that some *cis* unsaturation is present. In contrast, the spectrum of the polymer derived from ReCl<sub>5</sub> catalysis shown in D has only a weak absorption in the 970 cm<sup>-1</sup>

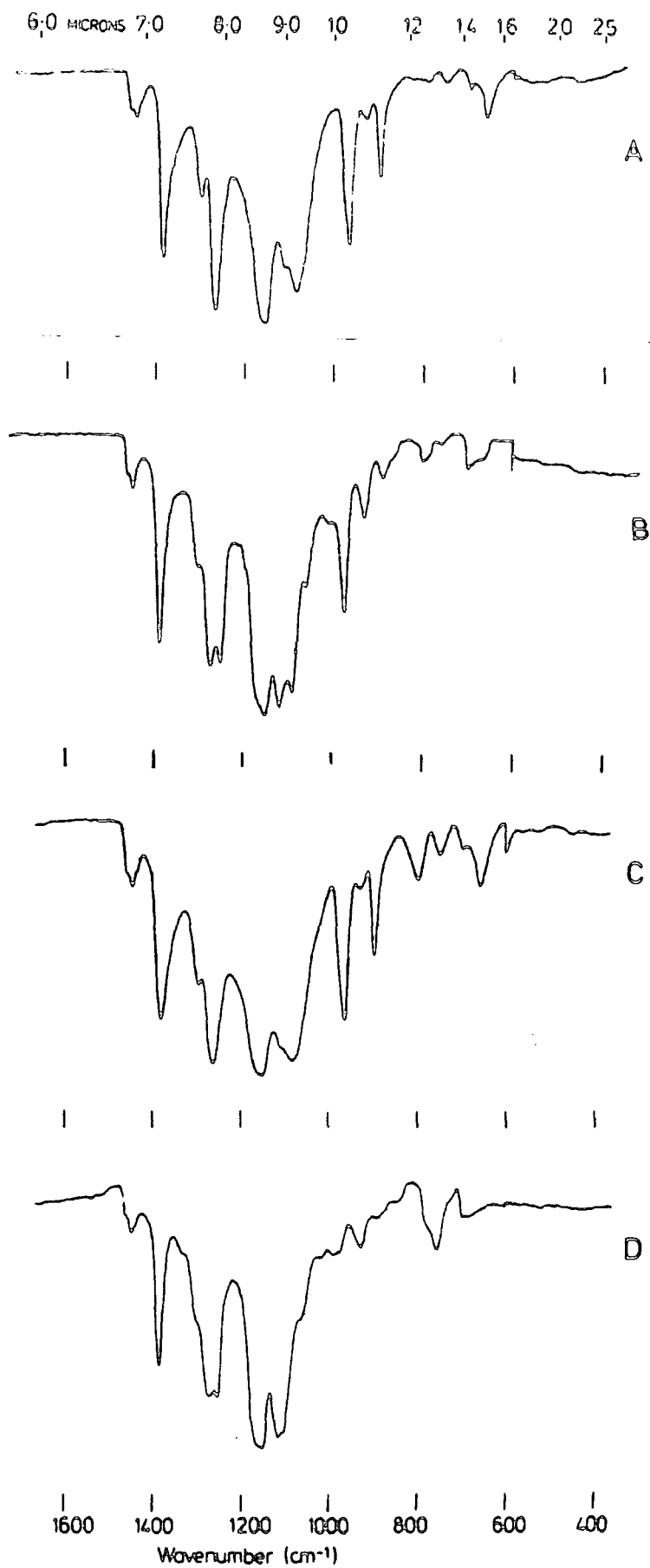
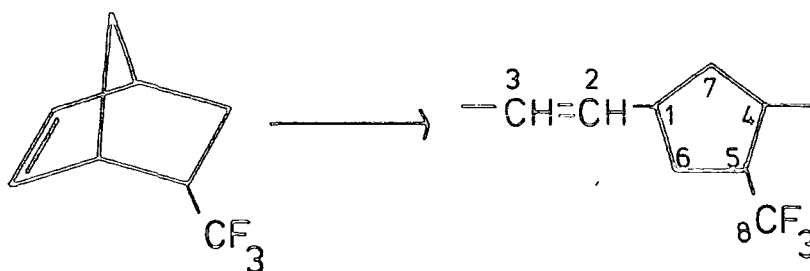


FIGURE 3.13 Infrared spectra of samples of poly(5-trifluoromethylnorbornene) prepared via different initiators.

region and a relatively intense absorption at  $730\text{ cm}^{-1}$ ; this polymer clearly has a high *cis* vinylene content.

(c)  $^{13}\text{C}$  N.m.r. of Polymers of exo and endo-5-trifluoromethylnorbornene

The  $^{13}\text{C}$  n.m.r. of the polymers obtained from ring opening of exo and endo-5-trifluoromethylnorbornene were obtained and are considered in order of increasing complexity. The structure of the polymer formed on ring opening and the numbering system used when assigning the spectra is shown below.



The polymer derived from osmium catalysed polymerization of the exo isomer gave the simplest  $^{13}\text{C}$  n.m.r. spectrum and is considered first. The spectrum is shown in Figure 3.14 and the shifts and assignments are recorded in Table 3.9. The resonance due to the carbon of trifluoromethyl group is easily distinguished as the quartet centred at 129.0 ppm ( $^1J_{\text{C-F}}=277\text{ Hz}$ ), which disappears in the DEPT spectrum. The remaining four signals at low field are assigned to the vinylene carbons corresponding to the TH and TT environments of C2, and the HT and HH environments of C3. The intensity of these signals is approximately equal which is consistent with an equal distribution of TH, TT, HH and HT assembly modes. Each  $\text{CF}_3$  group will exert a shift effect on carbons in the polymer chain depending on their proximity to the substituent. The position of peaks can be predicted by consideration of the  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  shift parameters, assuming they are additive.

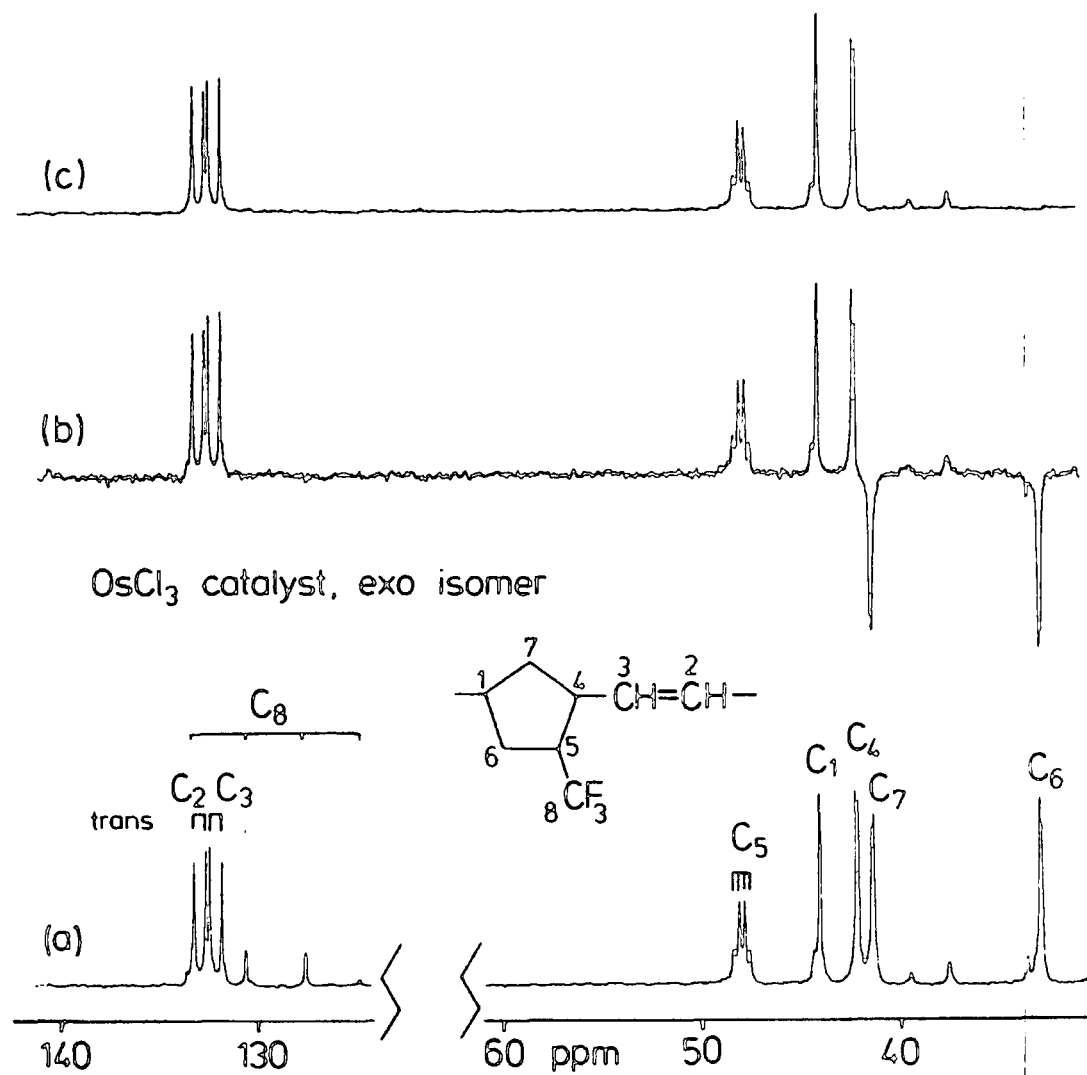


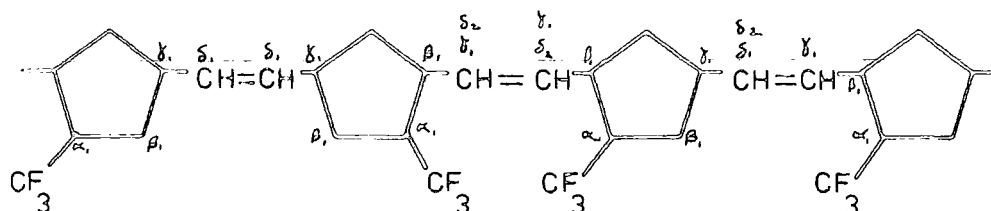
FIGURE 3.14 <sup>13</sup>C N.m.r. spectrum of the polymer prepared *via* OsCl<sub>3</sub> catalysis of exo-5-trifluoromethylbornene



TABLE 3.9  $^{13}\text{C}$  N.m.r. shifts and assignments of polymers of 5-trifluoromethylnorbornene

Shift/ppm				Assignment
Endo, $\text{OsCl}_3$	Endo, $\text{MoCl}_5$	Endo, $\text{ReCl}_5$	Exo, $\text{OsCl}_3$	
134.01	133.62		133.29	C2, t, TH
133.59		133.95		C2, c, TH
	133.09			
133.13		133.63		C2, c, TT
132.73	132.26	132.68	132.69	C2, t, TT
130.43	130.00			C3, t, HH
		130.43	132.48	
130.20	129.70			C3, t, HH
129.62		129.91		C3, c, HH
	129.06			
129.52		129.52		C3, c, HT
129.19	128.66	129.17	131.86	C3, t, HT
128.5 (q)	127.71 (q)	128.28 (q)	129.09 (q)	C8
$^1J_{\text{C-F}} = 281 \text{ Hz}$	$^1J_{\text{C-F}} = 279 \text{ Hz}$	$^1J_{\text{C-F}} = 277 \text{ Hz}$	$^1J_{\text{C-F}} = 277 \text{ Hz}$	
$\sim 46 \text{ (m)}$	$\sim 46 \text{ (m)}$	46.6 (m)	47.9 (q),	C5
			$^2J_{\text{C-F}} = 25.4 \text{ Hz}$	
43.50	43.38			C1, t
		43.37	43.94	
43.39	43.28			C1, t
41.96	41.75	41.82		C7, c
		41.47		C7, c
		41.06		C7, c
41.70	41.53		42.14	C4, t
			42.01	C4, t
40.21			41.46	C7, t
40.06			41.27	C7, t
		38.00		
37.81	37.03	37.63		
		37.36		C1/4c
		37.05		
34.06	33.77	34.09	32.89	C6, c
33.76	33.43	33.42	32.80	C6, c

Consideration of the substituent shift effects for the  $\text{CF}_3$  group shows that the chemical shift difference between the TH and TT signals ( $\delta_1 + \delta_2 - \delta_1 = \delta_2$ ) is the same as the HH and HT splitting ( $\gamma_1 + \delta_2 - \gamma_1 = \delta_2$ );  $\delta_1$  substituent effects are transmitted *via* single bonds and  $\delta_2$  effects *via* double bonds.



Assembly mode	TT	HH	TH	HT
carbon number	C-2	C-3	C-2	C-3
Substituent shift effect	$\delta_1$	$\gamma_1 + \delta_2$	$\delta_1 + \delta_2$	$\gamma_1$

The effect of methyl substitution on the chemical shifts of  $^{13}\text{C}$  nuclei is well documented. However, the substituent shift effect of a trifluoromethyl group in norbornene derivatives does not appear to be available. Two relevant sets of data have been found.<sup>157,158</sup>

$^{13}\text{C}$ n.m.r. shift (ppm)	$\text{C}_6\text{F}_{13}$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$
		31.4	20.6	29.7	29.7	29.7			
$^{13}\text{C}$ n.m.r. shift (ppm)	H	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$			
		14.4	23.4	32.7	30.2	30.5			
		$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$			
Effect of substitution (ppm) $\Delta$		17.0	-3	-3	-0.5	-0.8			
$^{13}\text{C}$ n.m.r. shift (ppm)	$\text{C}_6\text{F}_{13}$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{OH}$			
		31.9	18.1	33.1	62.7				
$^{13}\text{C}$ n.m.r. shift (ppm)	H	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{CH}_2$	$\text{OH}$			
		13.6	19.1	35.0	61.4				
		$\alpha$	$\beta$	$\gamma$	$\delta$				
Effect of substitution (ppm) $\Delta$		18.3	-1	-2	+1.3				

The above data illustrates the substituent shift of a perfluorohexyl group on the resonance position of carbon nuclei in a hydrocarbon chain, as compared to the simple H-substituted analogue. This rather limited data leads to the prediction that carbons  $\alpha$  to a trifluoromethyl group will experience a large downfield shift,  $\beta$  and  $\gamma$  carbons a small upfield shift and  $\delta$  carbons a small unpredictable shift. Unfortunately, as the  $\delta$  substituent shift effect can have either a positive or negative value prediction of the line order of the vinyl signals does not follow in a straightforward manner. Nevertheless, on inspection of the spectra of the polymers derived from the endo isomer, a splitting of the vinyl carbon resonance adjacent to the highest field signal is observed. This splitting is assigned to m and r dyads (see later) and is often associated with the HH signal. Assuming the same line order for the polymer derived from exo adduct, the resonance observed at 132.48 ppm (the second highest field signal of the vinyl set) in Figure 3.14 can therefore be assigned to the HH environment of C-3. The shift difference between the HH and HT, and TH and TT signals must be equal, and the only way this condition can be satisfied on the basis of the HH assignment, is to assign the highest field signal to the HT environment; (or alternatively the HT signal can be assigned to the lowest field signal, but the then enforced assignment of the TT and TH signals is not consistent with their substituent shift effects). The HT environment experiences a substituent shift effect of  $\gamma_1$ , and the HH environment a  $\gamma_1 + \delta_2$  effect. On the basis of the above assigned line order for these environments,  $\gamma_1$  must have a negative value.

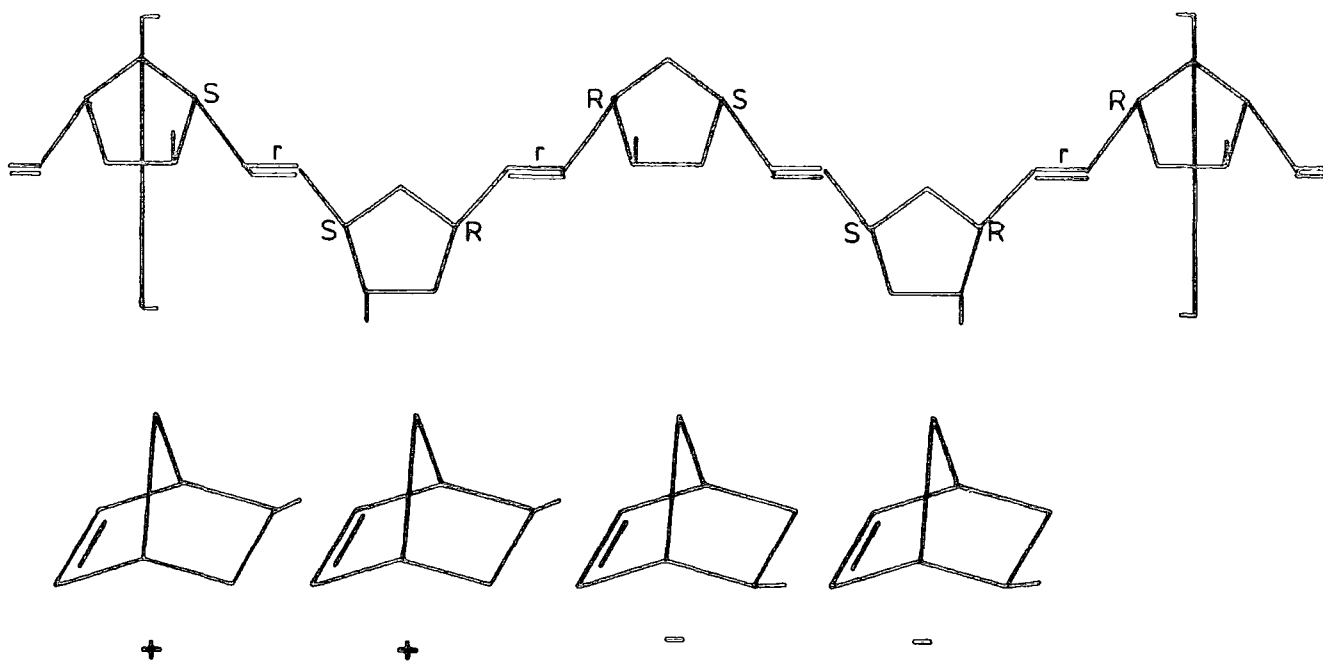
The assignment of the C-2 signals then follows in a routine manner; the TH environment which experiences a  $\delta_1 + \delta_2$  shift effect occurs at lowest field, and the HH resonance, with a  $\gamma_1 + \delta_2$  shift effect is adjacent to it and at higher field. The predicted line order is therefore C-2, TH, C-2, TT, C-3, HH and C-3 HT from low to high field, which is fortunately the same order derived for the methyl substituted case studied by Ivin and coworkers. Thus qualitative comparison of the spectra is possible.

The overall conclusion obtained from the vinyl carbon resonances of this polymer is that the number of HH, HT, TH and TT environments is equal. The infrared spectrum of this polymer indicates that it has a high *trans* content. The  $^{13}\text{C}$  n.m.r. shows that the polymer is all *trans* since the presence of any *cis* double bonds would increase the number of signals observed. The vinyl region of the spectrum does not show any resolution which can be attributed to m and r dyads; hence the polymer may be all m or all r, or m and r dyads are present but not resolved.

At high field the methylene and methine carbon signals were distinguished with the aid of the DEPT spectrum. The signal associated with C5 is identified as the quartet, at 47.9 ppm ( $^2J_{\text{C-F}}=25.4$  Hz). The signals due to C1 and C4 are assigned on the basis of the expected upfield shift for C4. The line order for the methylene carbons C6 and C7 are assigned as shown, by analogy with the spectra of polynorbornene and the expected substituent shift effect.

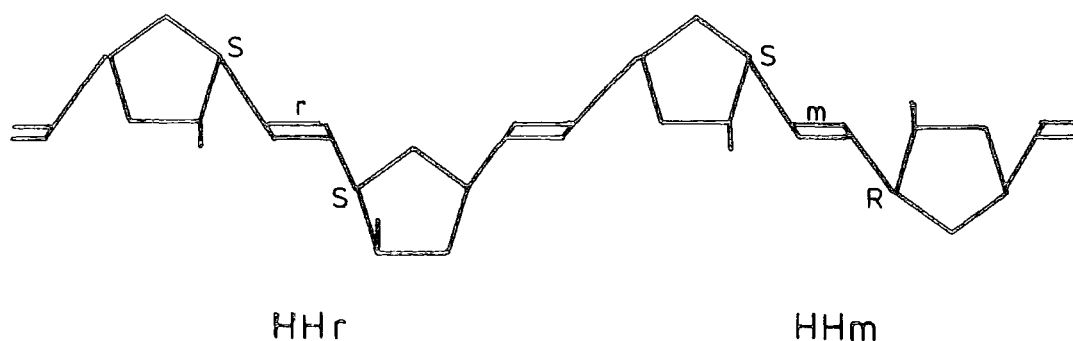
Each of the methylene and methine carbon resonances with the exception of C1, appear as two signals. The splitting is

attributed to head tail effects, which in the case of Cl is too small to resolve. The intensity of each line in each pair is approximately equal indicating that the number of TH, TT, HH and HT junctions is equal. The polymer, therefore, has an all *trans* stereochemistry with an equal distribution of TH, TT, HH and HT assembly modes. The remaining question relates to the distribution of m and r dyads. However, this cannot be unambiguously assigned on the basis of the information available. It is possible to write a stereoregular structure consistent with the spectrum, as shown below.



In this all *trans* syndiotactic structure there are equal concentrations of enantiomers of (IV) and equal numbers of TH, TT, HH and HT environments. However, this structure requires that enantiomers are incorporated in the sequence  $++--$ , which, although possible, seems unlikely. Hence, the overall conclusion from the analysis of the spectrum is that  $\text{OsCl}_3$  gives an all *trans*, atactic polymer, in which m and r dyads are unresolved.

The polymers derived from the endo isomer give more complicated spectra. Figure 3.15 shows the polymer obtained from the endo isomer using  $\text{OsCl}_3$  as catalyst. The infrared spectrum of this polymer indicates it has a high *trans* vinylene content. At low field, the carbon of the trifluoromethyl group is again easily identified as a quartet ( $^1J_{\text{C-F}} = 281\text{Hz}$ ). The olefinic resonance consists of four intense signals assigned to the TH and TT environments of C-2 and the HH and HT environments of C3; the basis of the assignment is analogous to that discussed earlier, although the magnitude of the substituent shift effect is different. In this case, however, the HH signal is resolved into m and r dyads. The splitting can be assigned to the HH assembly modes shown below which differ only in the orientation of the cyclopentane ring.



For HT, TH and TT environments the m/r splitting of the olefinic carbon resonances is too small to observe as a result of the insignificant difference in environment between the two forms. In contrast, in a HHr dyad the  $\text{CF}_3$  substituents are forced into close proximity, whereas in a HHm dyad they are reasonably well separated spatially. This must create a large enough difference in environment between the olefinic carbons in the two forms to allow them to be resolved as separate signals. These signals have slightly different intensities indicating that although the polymer is essentially

$\text{OsCl}_3$  catalyst, endo isomer

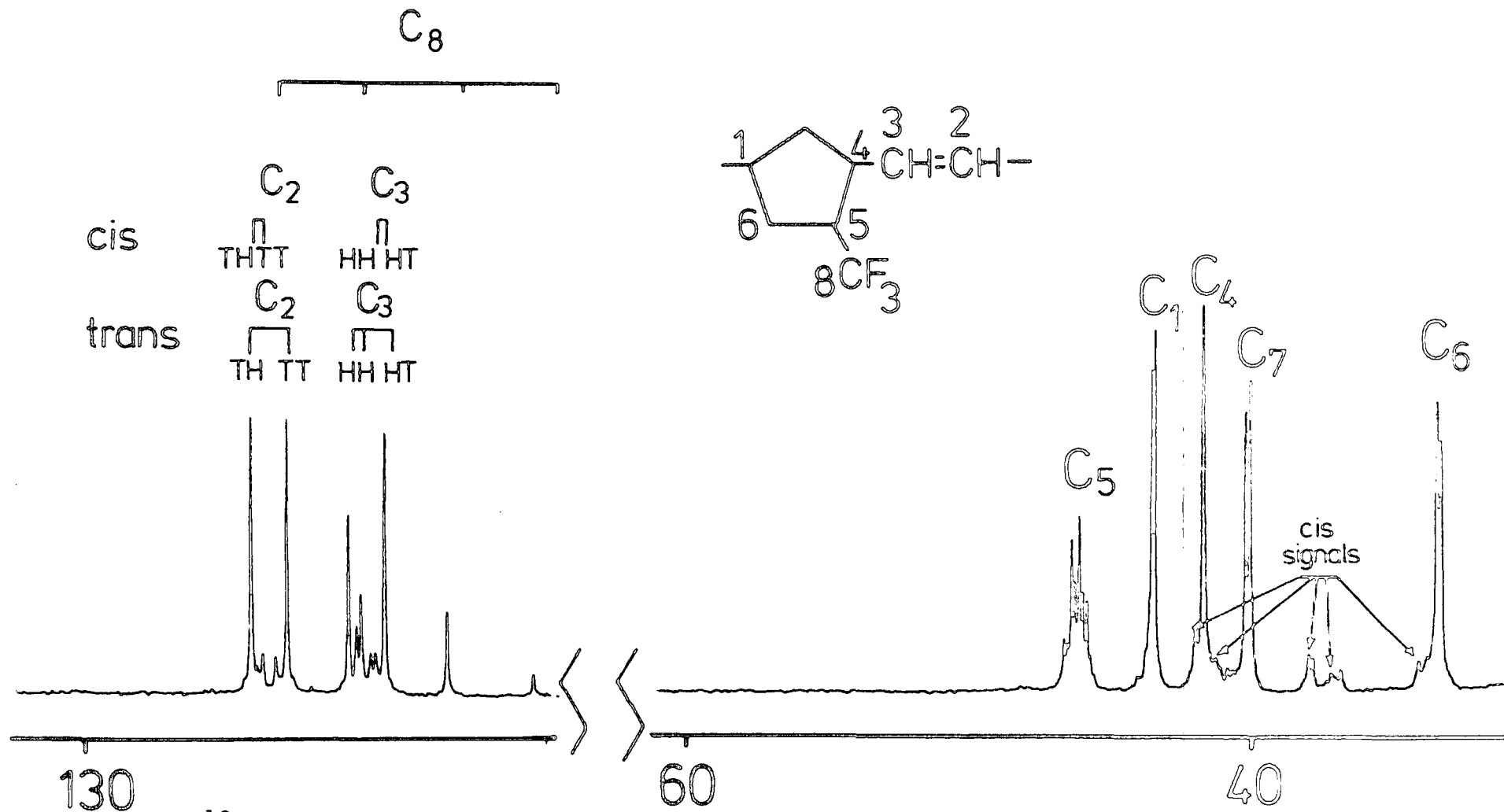


FIGURE 3.15  $^{13}\text{C}$  N.m.r. spectrum of the polymer prepared via  $\text{OsCl}_3$  catalysis of endo-5-trifluoromethylnorbornene

atactic there is a small measure of stereoselection. Consideration of the structures of the two dyads leads to the conclusion that the less strained HHm dyad is likely to predominate. For the polymer derived from polymerization of the exo isomer using  $\text{OsCl}_3$  catalyst there was no observable splitting of the HH signal, and it is clear that the stereochemistry of the substituent is important. Usually the effect is only observed in norbornene derivatives with two substituents in the 5-position, but occasionally the effect is observed where there is a single endo substituent. The TH/TT chemical shift difference for C2 is 1.31 ppm and the HH/HT splitting for C3 is 1.1ppm. A set of four relatively weak signals are also observed at low field, and are assigned to carbons associated with *cis* double bonds. The *cis* double bonds may have a random or blocky distribution along the polymer chain. If the distribution is random, then the *cis* signals observed are in fact ct signals, which should have a slightly different chemical shift from the cc peaks observed in high *cis* polymers. Alternatively, if there is a blocky distribution the weak peaks observed should superimpose on the high intensity signals in the spectrum of a high *cis* polymer. Figure 3.17 shows the spectrum of a high *cis* polymer (discussed later) and comparison with the spectrum of the high *trans* polymers indicates that the weak *cis* signals observed are slightly offset from the pure *cis* signals, indicating that they are ct peaks, and there is a random distribution of the small proportion of *cis* double bonds. This assignment is only tentative, and must be treated with caution since the small shifts involved could be a result of solvent or concentration effects. The value of  $\sigma_c$  calculated from



the vinylene carbon signals is 0.13; the accuracy of this value is questionable since the resolution of the spectrum is not good, and consequently the integration not very reliable.

The high field signals are assigned as depicted in Figure 3.15 by analogy with the earlier argument. The fine structure observed for the signals is attributed to HT effects. The low intensity signals observed in this region are assigned to carbons associated with *cis* double bonds, since they correspond to the high intensity signals observed in the spectrum of a high *cis* polymer. The overall conclusion from the analysis of the spectrum is that the polymer has a high *trans* vinylene content with an equal distribution of TH, TT, HH and HT junctions. The resolution of the vinylic HH resonance indicates that the polymer is essentially atactic. Since this polymer is atactic it seems likely that the analogous polymer derived from *exo* isomer is also atactic.

The spectrum of the polymer derived from  $\text{MoCl}_5$  catalysed polymerization of *endo*-5-trifluoromethyl norbornene is shown in Figure 3.16, and the chemical shifts and assignments recorded in Table 3.9. This spectrum is very similar to the polymer derived *via*  $\text{OsCl}_3$  initiation discussed previously, except the weak signals have now increased in intensity, and the resolution is not as good. At low field the *trans* HH peak is again resolved into two signals. The TH/TT shift difference is 1.3 ppm and the HH/HT difference is 1.2 ppm; these values are similar to those obtained for the high *trans* polymer derived from  $\text{OsCl}_3$  initiation. The intensity of the *trans* vinylene peaks indicates that the polymer has an equal distribution of TH, TT, HH and HT assembly modes.

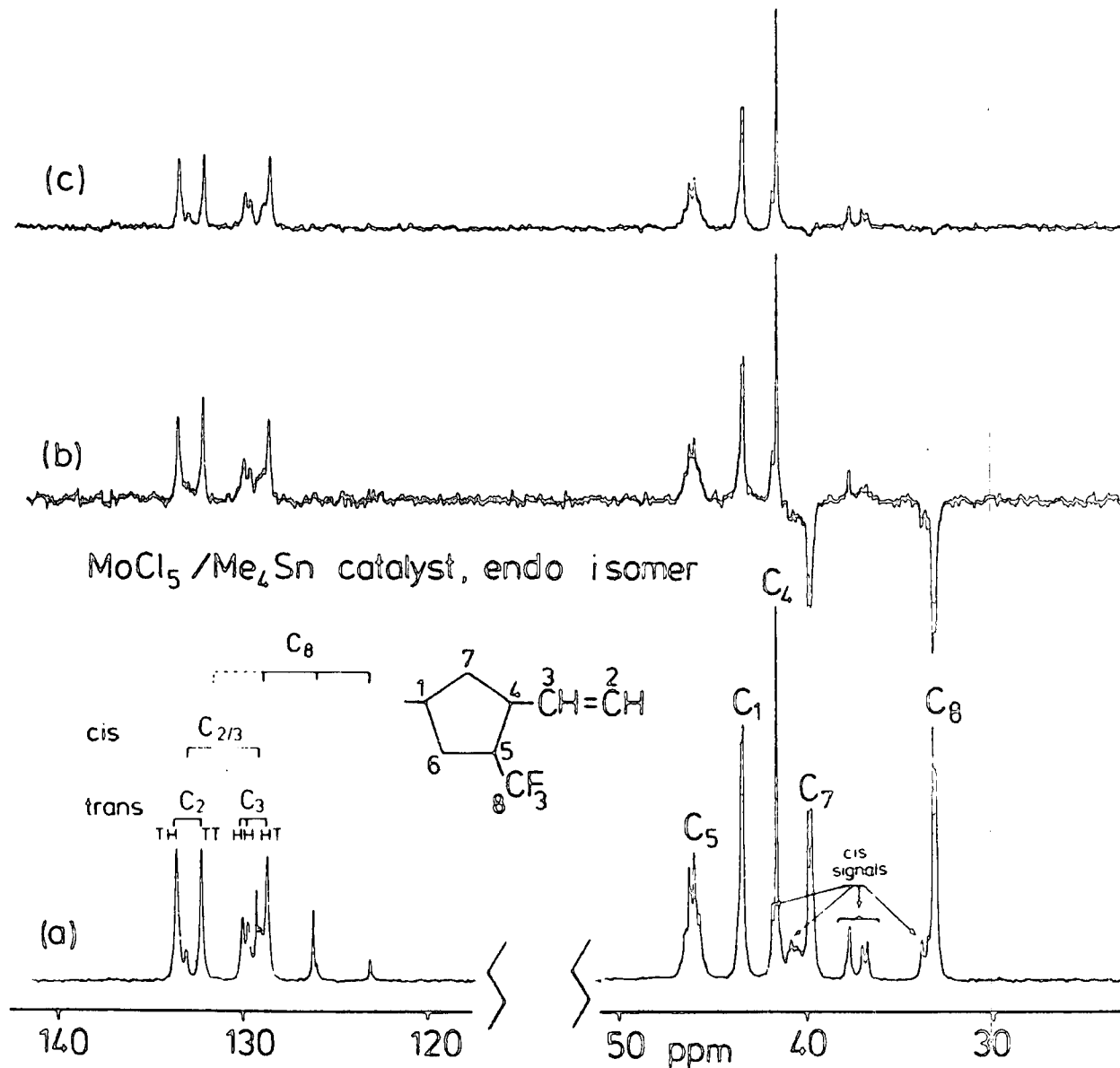


FIGURE 3.16 <sup>13</sup>C N.m.r. spectrum of the polymer prepared *via* MoCl<sub>5</sub>/Me<sub>4</sub>Sn catalysis of endo-5-trifluoromethylnorbornene

The weak peaks in this region are assigned to carbons associated with *cis* double bonds. The peaks are not well resolved and the *cis* TH peak is not observed or hidden by a strong, broadened *trans* peak. The  $\sigma_c$  value calculated from these signals is 0.12. However, comparison of Figure 3.15 and 3.16, and the infrared spectra, Figure 3.13, B and C, clearly indicates that the polymer derived *via*  $\text{OsCl}_3$  initiation has a higher *trans* content than the  $\text{MoCl}_5$  derived polymer and yet the  $\sigma_c$  value calculated from the spectrum was 0.13. This leads to the conclusion that the value of  $\sigma_c$  obtained for the  $\text{OsCl}_3$  derived polymer was an underestimate, or the value for the  $\text{MoCl}_5$  derived polymer an overestimate.

The high field signals are assigned by analogy with the spectrum of the high *trans* polymer made *via*  $\text{OsCl}_3$  initiation. The overall conclusion of the analysis of the  $^{13}\text{C}$  n.m.r. is that  $\text{MoCl}_5$  gives rise to a high *trans* atactic polymer.

The spectrum and assignments of the polymer derived from  $\text{ReCl}_5$  catalysis are shown in Figure 3.17, and the chemical shifts recorded in Table 3.9. The high intensity peaks in this spectrum correspond to the weak peaks observed in the spectra of the high *trans* polymers. Hence, it is clear that the polymer has a high *cis* content; this conclusion receives support from the infrared spectrum of the polymer. At low field the major peaks are assigned to the *cis* TH, TT, HH and HT environments. One of the inner limbs of the  $\text{CF}_3$  quartet overlaps with the HH and HT peaks making these signals correspondingly more intense. Taking this into account the TH, TT, HH and HT environments have approximately the same intensity, indicating that there is an equal distribution of these environments in the polymer chain. In the high *trans*

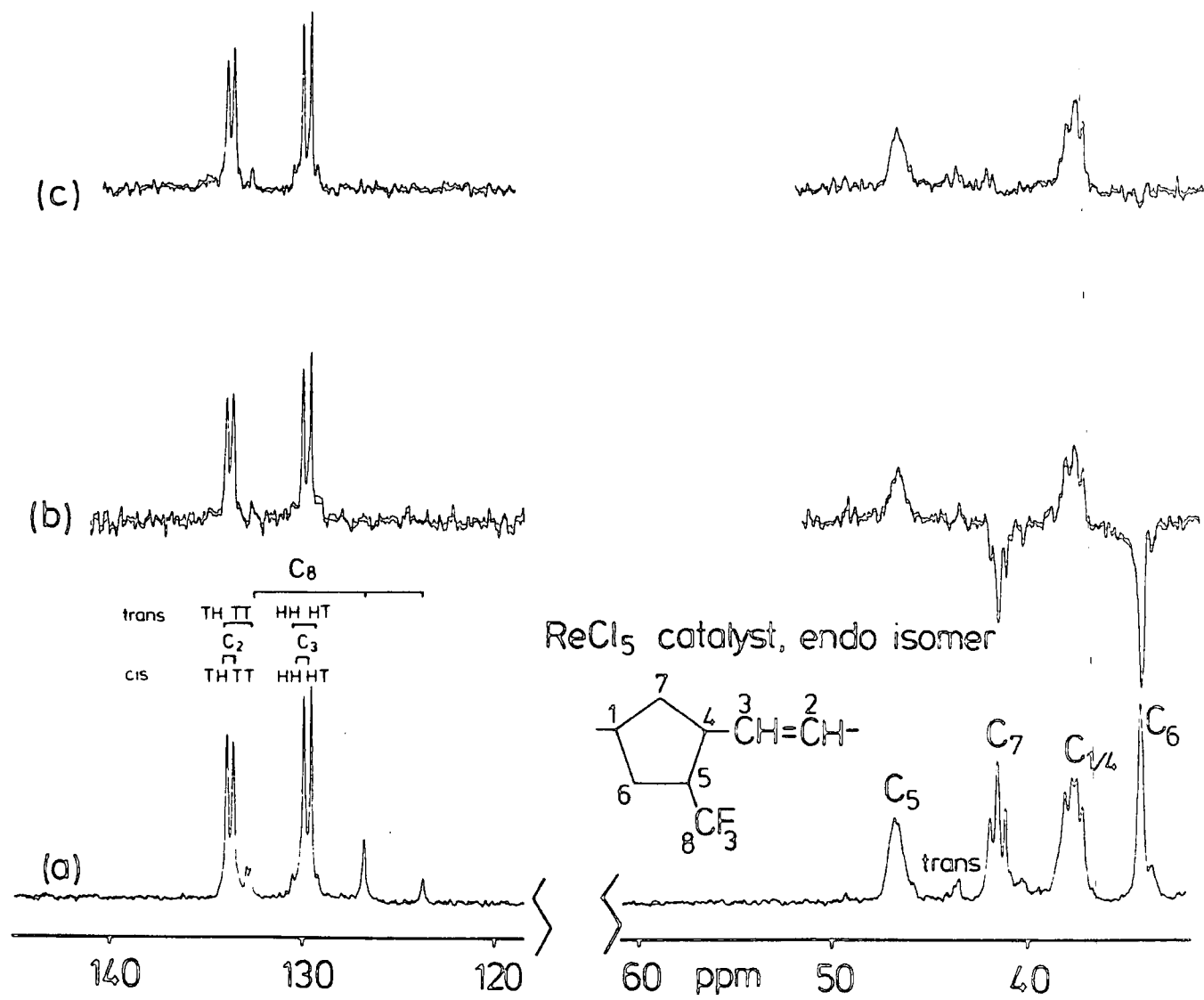


FIGURE 3.17 <sup>13</sup>C N.m.r. spectrum of the polymer prepared via ReCl<sub>5</sub> catalysis of endo-5-trifluoromethylnorbornene

polymers derived from  $\text{OsCl}_3$  and  $\text{MoCl}_5$  catalysis of the endo isomer, m and r dyads were present, as evidenced by the resolution of the olefinic HH resonance. In this example we see no such resolution and this leads to the conclusion that this polymer has an all meso or all racemic dyad assembly, although which tacticity cannot be determined on the basis of the available data. The weak intensity peaks observed in this region correspond to carbons associated with *trans* double bonds; the value of  $\sigma_c$  calculated from these signals is 0.92.

At low field the spectrum is very different from that of a high *trans* polymer. The C5 resonance appears at lowest field and is poorly resolved. The C-1 and C-4 resonances are identified with the aid of the DEPT spectrum. These signals overlap but the broad resonance appears to be resolved into four signals. These can be assigned to the HH and HT environments of C4, and the TT and TH environments of C-1. The C-6 resonance appears as a broad unresolved signal at highest field. The C-7 resonance appears as 3 signals in the ratio 1:2:1. There are four possible situations for this carbon arising from head/tail effects and observation of a triplet indicates coincidence of two environments. The weak intensity signals observed in this region are assigned to carbons associated with *trans* double bonds. The resolution of signals is not good enough to allow an accurate  $\sigma_c$  value to be calculated.

The overall conclusions to be drawn from analyses of the  $^{13}\text{C}$  n.m.r. spectra of these polymers is that, endo-5-trifluoromethylnorbornene gives an essentially stereoregular *cis* ( $\sigma_c=0.92$ ) polymer with  $\text{ReCl}_5$ , but it is not possible to deter-

mine whether the dyads are all *m* or all *r*; both  $\text{OsCl}_3$  and  $\text{MoCl}_5$  give high *trans* atactic polymers of endo-5-trifluoromethylnorbornene, and  $\text{OsCl}_3$  gives an all *trans*, atactic polymer of exo-5-trifluoromethylnorbornene.

### 3.7 Conclusions

2,3,-Bis(trifluoromethyl)norbornadiene, 2-trifluoromethylnorbornadiene and exo and endo-5-trifluoromethylnorbornene all undergo ring opening polymerization; the range of catalysts with which they do so is variable. The polymers produced could be purified to yield white granules, from which tough transparent films could be cast.

The polymers derived from  $\text{ReCl}_5$  catalysis of endo-5-trifluoromethylnorbornene and 2-trifluoromethylnorbornadiene are largely stereoregular. This catalyst fails to initiate the polymerization of 2,3-bis(trifluoromethyl)norbornadiene. This is believed to be a result of the bulky nature of the substituents which inhibits polymerizations leading to high *cis* vinylene contents. Polymers derived from Os, Ir, Ru and Mo based catalysts show varying degrees of *trans* vinylene selection, but all polymers were essentially atactic.

EXPERIMENTAL

### 3.8 Polymerizations

#### (a) Reagents

Analar chlorobenzene was purchased from B.D.H. Chemicals Ltd. The solvent was refluxed over  $P_2O_5$ , under a dry nitrogen atmosphere, and distilled when required. Tetramethyltin and trans-4-octene were purchased from Aldrich and used as supplied.  $WCl_6$  was prepared from  $WO_3$  and hexachloropropene, and stored and manipulated as described previously.<sup>88</sup>  $IrCl_3$  and  $ReCl_5$  were purchased from Ventron,  $OsCl_3$ ,  $RuCl_3$  and  $MoCl_5$  were purchased from Aldrich. All catalysts were used as supplied.

#### (b) Polymerization procedure

A dry nitrogen/vacuum line of the type depicted in Appendix A was used in order to carry out all manipulations of catalysts under a dry nitrogen atmosphere. The front manifold was connected to the vacuum pump, and the back manifold to a dry nitrogen supply. The nitrogen was passed through a concentrated sulphuric acid bubbler into the line, and out through a heavy white oil bubbler. Teflon taps and greasefree joints were used throughout. A piece of apparatus connected at (1) may be evacuated by opening tap (2) and any other taps leading to the vacuum pump. Once evacuated tap (2) is closed and tap (3) opened slowly whilst watching the heavy white oil bubbler, and adjusting the rate at which the tap is opened to prevent suck back of air into the system.

All glassware was dried in an oven for at least 12 hours before use, evacuated whilst still hot and let down to dry nitrogen. Syringes were dried in the oven, and allowed to



cool in a desiccator.

A flask of type 1, (Appendix A), was used to make up the catalyst solution. The preweighed flask was placed in a glove box, and catalyst added by removing the teflon tap. A solids funnel is used to prevent contamination of the joint with catalyst. The flask was removed from the glove box, weighed, and connected to the vacuum line. The region from the socket to the teflon tap was evacuated and let down to nitrogen. The tap could then be removed and replaced by a septum seal, and the required amount of solvent then added using an airtight syringe.

A flask of type 2, (Appendix A), was used as the reaction vessel. The ground glass joints were closed with septum seals. A dry teflon coated magnetic follower was inserted into the flask, after removing one of the seals, against a counter current of nitrogen. The required amount of purified monomer and solvent was added to the flask and degassed by manipulation of the appropriate taps. After several freeze-thaw cycles the flask was let down to nitrogen and stirred. The required volume of catalyst solution was transferred from flask (1) to flask (2) using an airtight syringe, *via* the septum seals. The reaction mixture was stirred, and heated if required.

In cases where the catalyst required activation a flask of type 3, (Appendix A), was used. The joint was closed with a septum seal, and the flask evacuated, let down to dry nitrogen and a magnetic follower inserted. The required volume of catalyst solution and activator were added to the flask, *via* the septum seal, and stirred for the appropriate

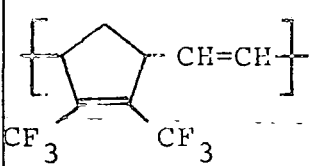
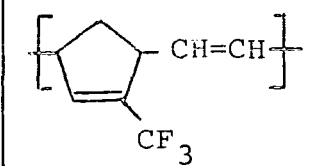
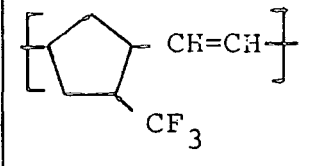
period (usually 2 minutes). The activated catalyst solution was then transferred, *via* a syringe to the reaction vessel. The polymerization was terminated by the addition of 2-3 cm<sup>3</sup> of methanol.

The details of the catalyst and monomer concentrations, reaction times and yields, *etc.*, are given in the text.

(c) Purification of polymers

After termination of the polymerization reaction, the mixture was added to a large excess of non-solvent causing the polymer to precipitate. The polymer was recovered, dried under vacuum and dissolved. The polymer solution was reduced in volume on a rotary evaporator, to give a viscous solution and then added dropwise to the stirred non-solvent. These manipulations were carried out under a nitrogen atmosphere as far as possible. The polymer was recovered, dried, and the process repeated until clean, white polymer was obtained. Table 3.10 lists the solvents and non solvents for each polymer obtained.

TABLE 3.10 Solvents and non-solvents for polymers of monomers (I), (II), (III) and (IV) prepared via different initiators

	Catalyst	Solvent	Non-solvent
	WCl <sub>6</sub> /Me <sub>4</sub> Sn	acetone	hexane or pentane
	MoCl <sub>5</sub> /Me <sub>4</sub> Sn	"	"
	RuCl <sub>3</sub>	"	"
	RuCl <sub>3</sub> /Me <sub>4</sub> Sn	"	"
	WCl <sub>6</sub> /Me <sub>4</sub> Sn	acetone	methanol
	MoCl <sub>5</sub> /Me <sub>4</sub> Sn	"	methanol
	RuCl <sub>3</sub>	"	hexane
	OsCl <sub>3</sub>	"	methanol
	IrCl <sub>3</sub>	"	methanol
	ReCl <sub>5</sub>	"	methanol
	OsCl <sub>3</sub> (exo)	acetone	methanol
	OsCl <sub>3</sub> (endo)	acetone	methanol
	MoCl <sub>5</sub> /Me <sub>4</sub> Sn (endo)	chloroform	methanol
	ReCl <sub>5</sub> (endo)	acetone	methanol

CHAPTER FOUR

METATHESIS POLYMERIZATION OF A RANGE  
OF FLUORINATED NORBORNENE DERIVATIVES

#### 4.1 Introduction

This chapter is concerned with the polymerization of monomers (V)-(X) as part of an investigation into the range of compounds susceptible to the ring-opening metathesis reaction. The microstructure of the polymer chains was investigated using  $^{13}\text{C}$  n.m.r. and infrared spectroscopy, as described previously, and in addition gel permeation chromatography data was obtained.

#### 4.2 Polymerization of 5-bromotetrafluoroethylnorbornene(V)

##### (a) Catalysts effecting the polymerization of (V)

5-Bromotetrafluoroethylnorbornene was synthesised as a mixture of exo and endo isomers, which could not be separated by gas chromatography with any of the available stationary phases; hence the monomer was polymerized as a mixture. The details of the polymerizations are given in Table 4.1

TABLE 4.1 Polymerization of 5-bromotetrafluoroethylnorbornene

Monomer (mmole)	Catalyst (mmole)	Cocatalyst (mmole)	Solvent <sup>a</sup> (cm <sup>3</sup> )	Temp <sup>b</sup> (hrs)	Time (hrs)	Yield <sup>c</sup> (%)
37.76	WCl <sub>6</sub> (0.18)	Me <sub>4</sub> Sn (0.36)	C, (5)	RT	2 min	82
11.98	MoCl <sub>5</sub> (0.06)	Me <sub>4</sub> Sn (0.12)	C, (1.6)	RT	2 min	67
12.72	RuCl <sub>3</sub> (0.06)	Me <sub>4</sub> Sn (0.12)	CE, (1.6)	50	24	41
17.79	ReCl <sub>5</sub> (0.09)	Me <sub>4</sub> Sn (0.18)	C, (3.3)	50	36	10

a. C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.

b. Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.

c. After reprecipitation and drying under vacuum for at least 24 hours.

Clearly monomer(V) can be readily polymerized. The polymer produced *via*  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  initiation was insoluble, but when the polymerization was repeated in the presence of *trans*-4-octene, as a chain transfer agent, the resulting polymer was easily dissolved.

(b) Infrared spectra of polymers of (V)

The infrared spectra of samples of poly(5-bromotetrafluoroethylnorbornene) prepared *via* different initiators are shown in Figure 4.1. The spectra of the W, Mo and Ru derived polymers, although prepared from different thicknesses of film, are very similar. In particular, all show absorptions at both  $750$  and  $970\text{ cm}^{-1}$ , although the relative intensity of the  $750\text{ cm}^{-1}$  absorption in each, cannot be distinguished due to the overlap of other peaks. Comparison of the intensity of the  $970\text{ cm}^{-1}$  peak with a band which remains constant in intensity, *e.g.* the absorption at  $930\text{ cm}^{-1}$ , leads to the conclusion that the *trans* vinylene content increases in the order  $\text{Ru} > \text{Mo} > \text{W}$ . In contrast, for the polymer derived *via*  $\text{ReCl}_5$  initiation, the band at  $970\text{ cm}^{-1}$ , although still present, has become very weak, and the  $750\text{ cm}^{-1}$  absorption correspondingly intense. Hence, it seems likely that the W, Mo and Ru derived polymers have variable amounts of *cis* and *trans* double bonds, whereas the  $\text{ReCl}_5$  derived polymer has a high *cis* vinylene content.

(c)  $^{13}\text{C}$  N.m.r. spectra of polymers of (V)

5-Bromotetrafluoroethylnorbornene is a chiral molecule existing as equal amounts of (+) and (-) enantiomers. In addition, the monomer is a combination of *exo* and *endo* isomers. Hence, the monomer is essentially a mixture of four

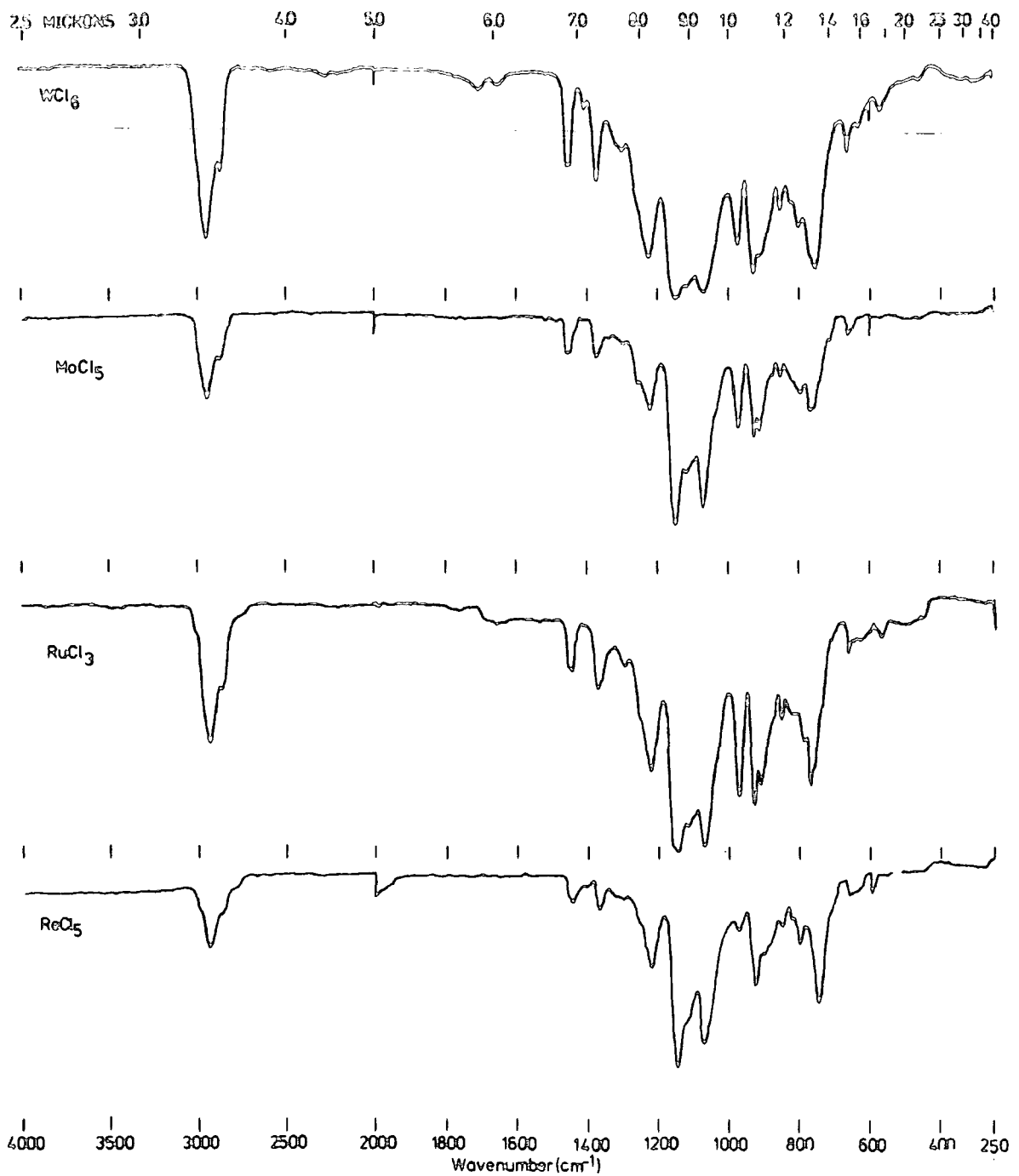


FIGURE 4.1 Infrared spectra of samples of poly(5-bromo-tetra-fluoroethylnorbornene) prepared via different initiators

compounds, and consequently it would be expected that the  $^{13}\text{C}$  n.m.r. spectra of polymers derived from it would be complicated, except in cases where there was some catalyst selection.

The spectra of the polymers obtained from  $\text{ReCl}_5$  and  $\text{RuCl}_3$  catalysis are shown in Figures 4.2 and 4.3 respectively. From comparison of the figures it is evident that both catalysts give rise to polymers with complicated spectra, but also that some signals present in the spectrum of the  $\text{RuCl}_3$  derived polymer are totally absent from the spectrum of the polymer obtained from  $\text{ReCl}_5$  initiation, and *vice versa*. The spectrum of the polymer obtained *via*  $\text{MoCl}_5$  catalysis is poorly resolved, and not shown, but is very similar to Figure 4.3, except some extra, weak intensity peaks have appeared. The  $\text{WCl}_6$  derived polymer gave the most complex spectrum, giving signals at positions coinciding with the shifts of peaks observed in the spectra of both the Ru and Re derived polymers. From this brief consideration of the  $^{13}\text{C}$  n.m.r. spectra, and the results of examination of the infrared spectra, it can be concluded that;  $\text{ReCl}_5$  gives a polymer with an all *cis* vinylene content; the  $\text{RuCl}_3$  derived polymer has an all *trans* vinylene content; the polymer derived from  $\text{MoCl}_5$  has a high *trans* vinylene content; and the  $\text{WCl}_6$  polymer contains a mixture of *cis* and *trans* double bonds.

The spectrum of the  $\text{ReCl}_5$  derived polymer is complicated, but an attempt has been made to assign the signals. The repeat unit and numbering system is shown in Figure 4.4.



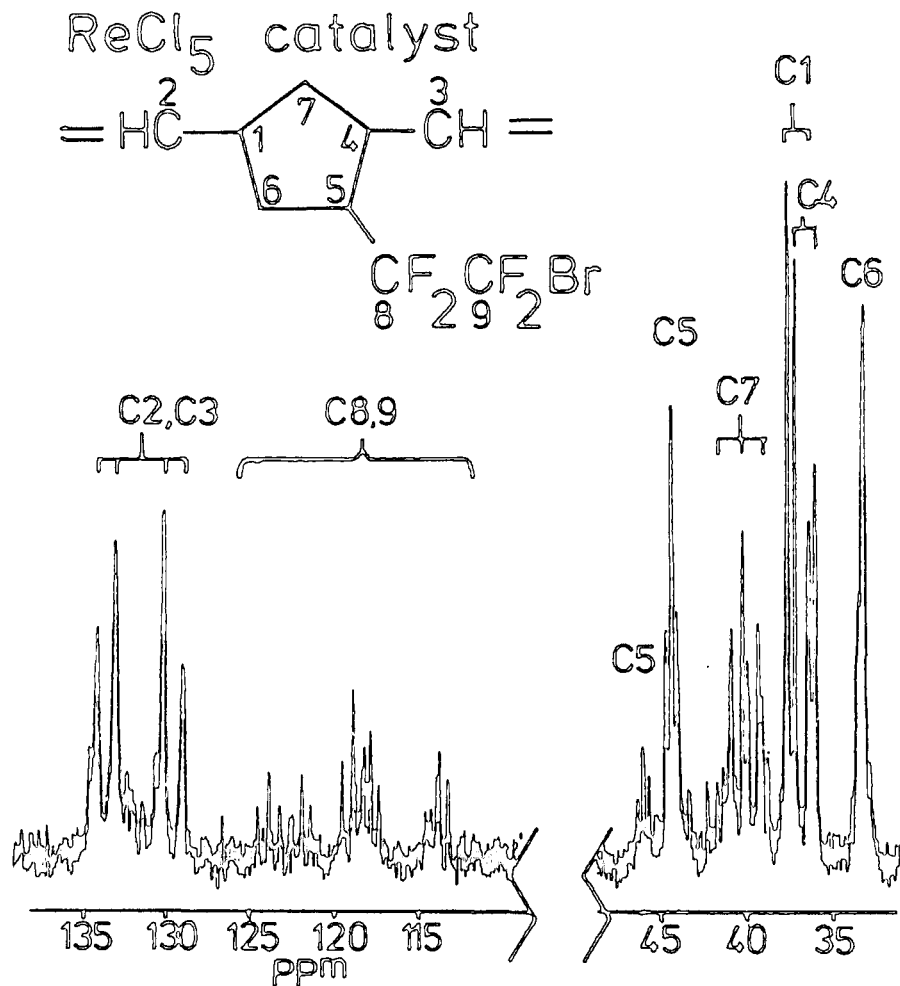


FIGURE 4.2 <sup>13</sup>C N.m.r. spectrum of poly(5-bromotetrafluoroethylnorbornene) prepared via ReCl<sub>5</sub> initiation

RuCl<sub>3</sub> catalyst

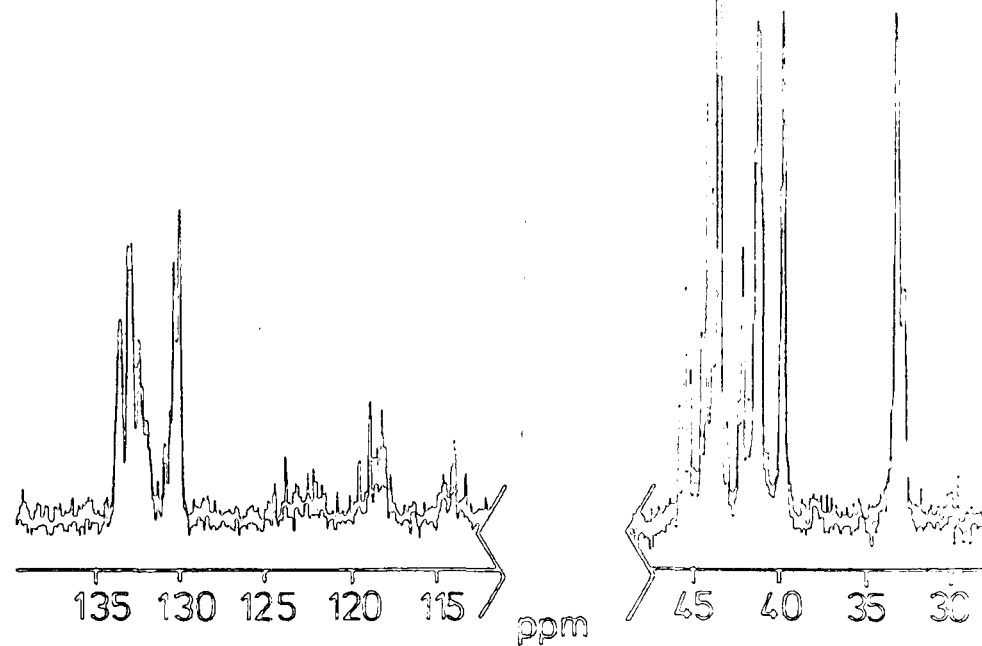
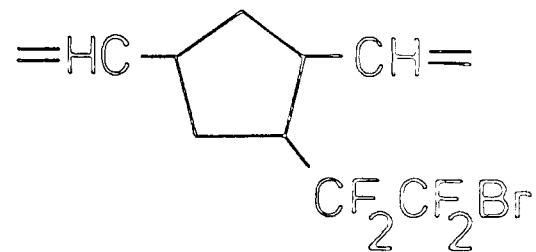


FIGURE 4.3 <sup>13</sup>C N.m.r. spectrum of poly(5-bromotetrafluoroethylnorbornene) prepared via RuCl<sub>3</sub> initiation

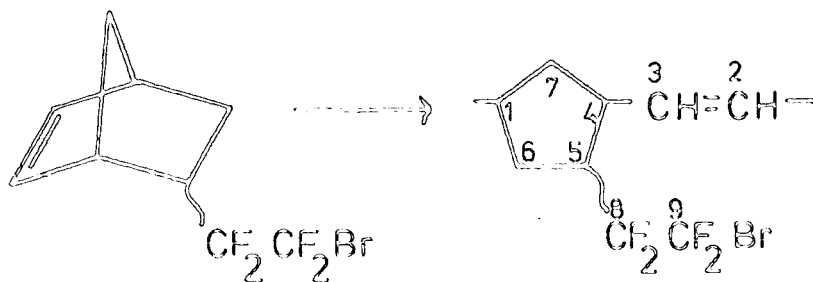


FIGURE 4.4 Ring opening polymerization of 5-bromotetrafluoroethylnorbornene

The peaks in the spectrum are associated with *cis* vinylene units. At the low field region of the spectrum the C8 and C9 signals are easily identified as low intensity overlapping triplets in the range 113-124 ppm. The remaining signals in this region are assigned to the vinyl carbons, C2 and C3. There are four high intensity signals observed and it is possible to assign these to the *cis* TH, HH, TT and HT environments. The substituent shift effect of a bromotetrafluoroethyl group does not appear to be available in the literature. If it is assumed that the order of vinylene carbon signals is the same as for a trifluoromethyl substituent, then the signals from low to high field are attributed to the TH, TT, HH and HT environments. Since the two central signals have a higher intensity than the outer signals, it seems there is a slight bias towards head-head, tail-tail assembly modes. However, why there should be a bias of this sort is not clear. In hydrocarbon poly(norbornenes) HH/TT bias is observed for monomers of high optical purity, when this is the only way in which the particular enantiomer can be incorporated into a *cis* syndiotactic sequence. In cases where HT bias is observed

for a racemic monomer, steric restrictions in the transition state are postulated to be responsible for the selectivity. Consideration of the transition state required to form a HH unit in high *cis* poly(5-bromotetrafluoroethyl-norbornene) does not provide a rationale for the apparent selectivity observed. Indeed, steric restrictions in the polymer chain, in which the  $-\text{CF}_2\text{CF}_2\text{BR}$  substituents are *cis* to each other, and situated over the double bond, seem to imply that a HH junction would be unfavourable. It may be that the assignment is incorrect, and the line order is not, as has been assumed, the same as that in poly(trifluoromethylnorbornene). If this is the case, since the number of HH junctions must equal the TT assemblies, the outer signals are assigned to these environments, and the inner signals to the HT and TH environments. In this assignment, there is a slight HT bias, and on steric grounds, it seems likely that this assembly would be preferred. Overall, an unambiguous assignment of these signals is not possible, and in any event, the extent of bias is small. Assuming the line order is the same as for poly(trifluoromethylnorbornene) the observed TH/HH splitting is 1.04 ppm, and the TT/HT splitting is 1.16 ppm. The signals are attributed to carbons associated with repeat units derived from endo monomer. The substituent shift effect of an exo-bromotetrafluoroethyl substituent would be different from an endo, and give signals at different chemical shifts; the weak intensity signals are possibly a consequence of this or alternatively could be attributed to carbons associated with a low concentration of *trans* double bonds.

At high field, two sets of signals, resolved into three lines with approximately 1:2:1 intensity, are observed.

These are assigned to C5 carbons in units derived from endo and exo monomers and are triplets with a coupling constant of  $\approx 20\text{Hz}$ , as expected for an  $\alpha\text{-CF}_2\text{-}$  substituent. The ratio of these signals indicates that the polymer chain consists of 88% of units derived from endo monomer. Since the monomer mixture had a 75:25 ratio of endo:exo isomers, it seems there has been a marginally selective incorporation of endo units into the polymer. The resonance at highest field can be assigned to C6, by comparison with the spectra of poly(5-trifluoromethylnorbornene); this signal appears to be partially resolved into two lines, which is consistent with head tail splitting. The remaining signals in this region are more difficult to assign. However, the four peaks observed at 36.20, 36.57, 37.41 and 37.84 ppm can be confidently assigned to *cis* methine carbon signals, since these peaks are totally absent from the spectrum of the  $\text{RuCl}_3$  derived polymer. The total integral of these peaks indicates that the signals can be attributed to both carbons 1 and 4. It is possible that the signals at 37.84 and 36.57 ppm are associated with the TT and TH environments of C1, and those at 37.41 and 36.20 ppm attributed to the HH and HT environments of C4. The different intensity of the TT resonance as compared to the TH peak, (and the HH signal with the HT signal) is again consistent with there being a small degree of bias in the polymer chain. However, which signal corresponds to the TT resonance, and which represents the TH environment, cannot be assigned with certainty; hence whether there is head-tail, or head-head/tail-tail bias remains unresolved. The remaining signals in this region are assigned to the methylene carbon, C7;

the integral of these peaks is consistent with their being assigned to one carbon. The peak appears as three lines, which can be attributed to the four possible environments of C7, as shown in Figure 4.5, where the middle signal represents coincidence of two environments.

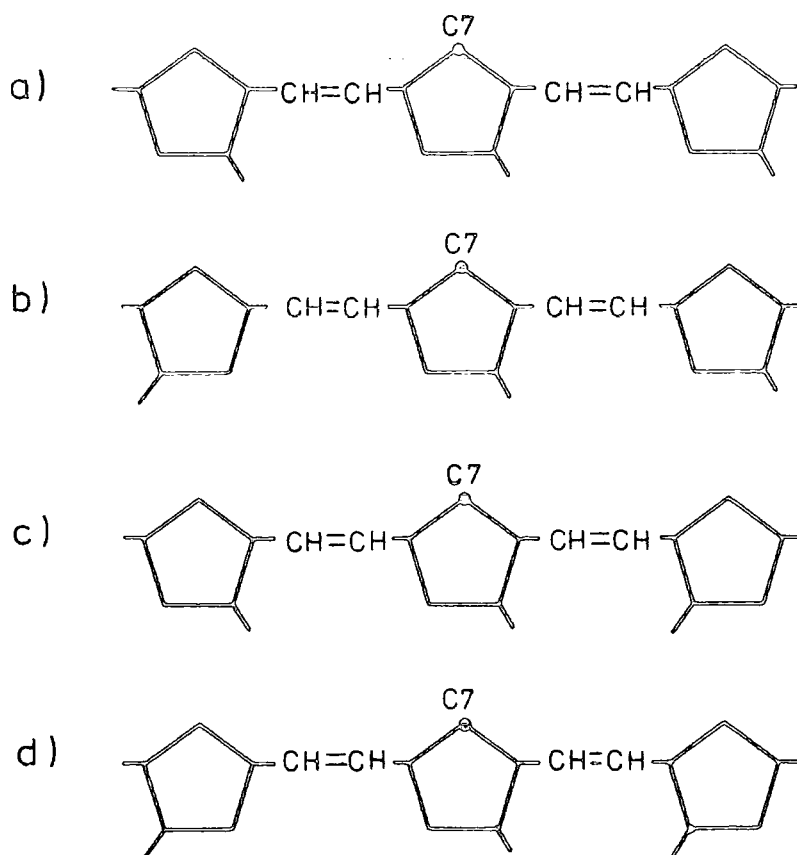


FIGURE 4.5 Different environments for Carbon 7

The further resolution observed for two of these signals can only be a result of  $m/r$  splitting, since HT effects are unlikely to be transmitted further down the chain. The  $m$  and  $r$  environments of structures (c) and (d) are the most likely to be resolved, since it is in these assemblies that HH junctions are formed. If the highest field signal of the set is assigned to the  $m$  and  $r$  environments of (d), and the middle signal to the  $m$  and  $r$  environments of (c), then

the increased intensity of the signal due to (c) is a result of overlap of the resonance associated with (a). The lowest field signal, which is unresolved, is then assigned to (b). The difference in intensity of the m and r signals suggests there is a slight degree of selectivity. For the vinylene carbons, HH resonances are sometimes resolved into m and r environments. However, in this polymer there was some uncertainty over the assignment of the different signals, and hence m and r resolution is difficult to differentiate with certainty, although it is probable that the resonance at 130 ppm corresponds to the HH C3 environment and shows m/r splitting. Thus, the low field signals do not provide conclusive evidence that our assignment of the C7 signals is correct.

An alternative explanation of the observed resolution of the C7 resonance is that the weaker resonances are attributed to carbons derived from exo isomer, although their intensity appears too great for this. Unfortunately, from the data available it is not possible to determine which assignment is correct.

The overall conclusion to be drawn from analysis of the  $^{13}\text{C}$  n.m.r. spectrum is that  $\text{ReCl}_5$  gives rise to a polymer with an all *cis* vinylene content, in which there has been selective incorporation of endo monomer. There is a slight head-tail, or head-head/tail-tail bias in the polymer chain, but it is not possible to tell which. One postulate for the assignment of the methylene carbon signals is also consistent with a small degree of selectivity.

The assignment of signals in the spectrum of the sample derived from  $\text{RuCl}_3$  initiation has so far defied a thorough interpretation. The C5 resonances are again easily identified as a pair of triplets centred at 45.53 and 44.24 ppm. The ratio of these signals indicates that the endo and exo isomers have been incorporated into the polymer chain in the ratio 70:30. Since the monomer consisted of a 75:25 endo:exo mixture, there has been little apparent preferential incorporation of either isomer. The absence of signals in the region 36-38 ppm, where *cis* carbon signals would be observed, and the presence of signals at *ca.* 43 ppm, indicates the polymer has an all *trans* vinylene content. The complexity of the spectrum suggests it is atactic. By analogy, the Mo and W derived polymers are also probably atactic, since both give similarly complex spectra.

#### 4.3 Polymerization of 5-pentafluorophenylnorbornene (VI)

##### (a) Catalysts

5-Pentafluorophenylnorbornene was polymerized as a mixture of exo and endo isomers. The details of the polymerization are given in Table 4.2.

The monomer was readily polymerized by all catalysts used.

TABLE 4.2 Polymerization of 5-pentafluorophenylnorbornene

Monomer (mmole)	Catalyst (mmoles)	Cocatalyst (mmole)	Solvent <sup>a</sup> (cm <sup>3</sup> )	Temp <sup>b</sup> (°C)	Time (hrs)	Yield <sup>c</sup> (%)
6.26	WCl <sub>6</sub> (0.031)	Me <sub>4</sub> Sn (0.062)	C, (6.2)	RT	2 mins	86
2.50	MoCl <sub>5</sub> (0.012)	Me <sub>4</sub> Sn (0.024)	C, (3.3)	RT	2 mins	85
13.19	RuCl <sub>3</sub> (0.066)	Me <sub>4</sub> Sn (0.132)	CE, (4.4)	45	12	20
17.03	ReCl <sub>5</sub> (0.085)	Me <sub>4</sub> Sn (0.17)	C, (3.1)	55	24	24

- a. C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.
- b. Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.
- c. After reprecipitation and drying under vacuum for at least 24 hours.

(b) Infrared spectra of polymers of (VI)

The infrared spectra of samples of poly(5-pentafluorophenylnorbornene) prepared *via* different initiators are shown in Figure 4.6. Unfortunately the spectra, which are not well resolved, are dominated by an intense absorption in the 1000 cm<sup>-1</sup> region. Hence, no useful information could be obtained from the out of plane bending mode of a *trans* double bond. Comparison of the intensity of the band at 730 cm<sup>-1</sup> suggests that the polymers derived from Re, W and Mo catalysts have significant proportions of *cis* vinylenes, whereas the Ru derived polymer has a low *cis* content.

(c) <sup>13</sup>C N.m.r. spectra of Polymers of (VI)

The monomer, as before, is essentially a mixture of four compounds, and hence relatively complicated n.m.r. spectra were obtained for its polymers. The spectra of the Mo and Re



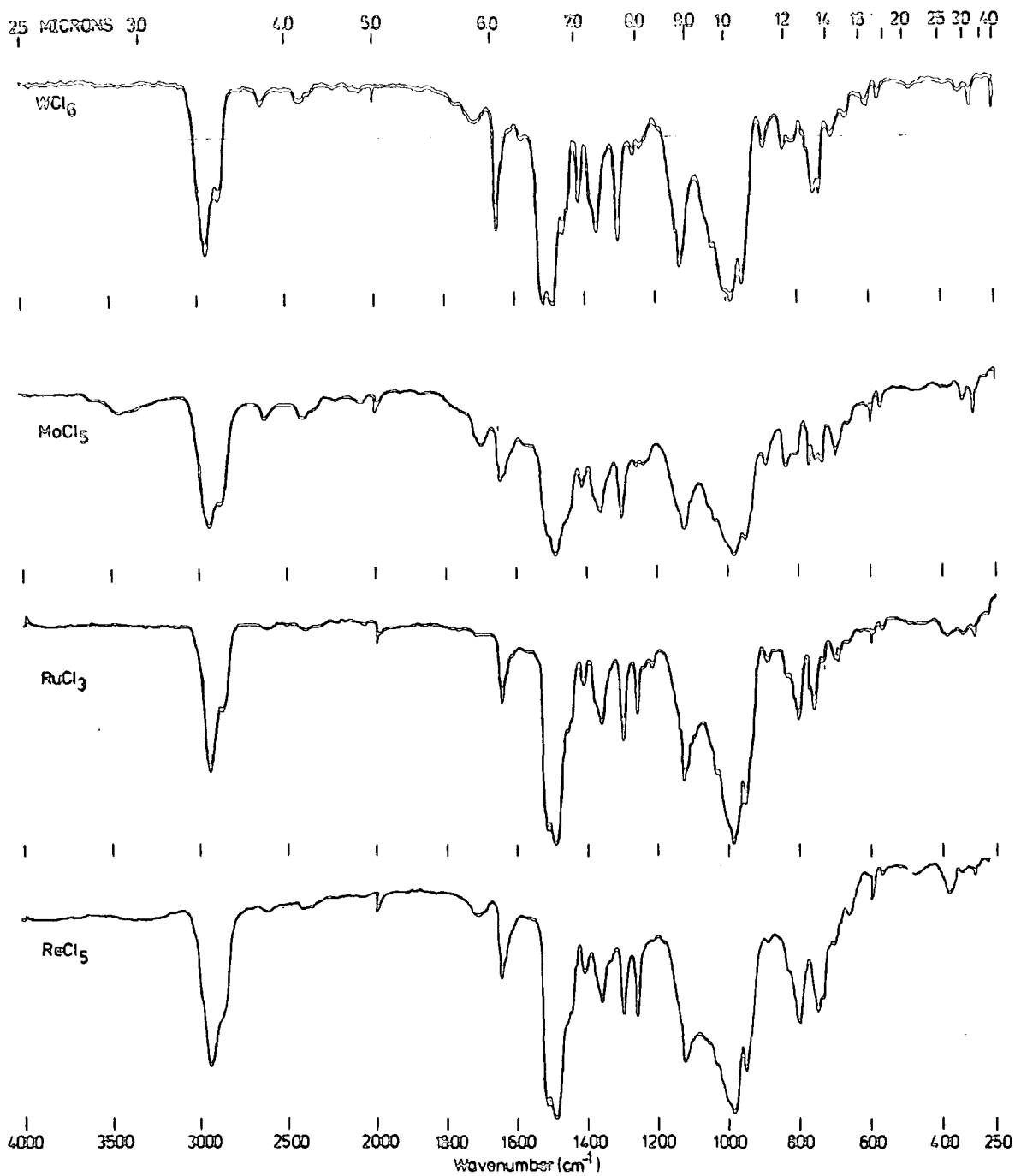


FIGURE 4.6 Infrared spectra of samples of poly(5-pentafluorophenylnorbornene) prepared via different initiators

derived polymers are shown in Figures 4.7 and 4.8 respectively; a detailed analysis of these complicated spectra proved impossible. However, comparison of the two spectra shows that large differences are observed. In the spectrum of the  $\text{ReCl}_5$  derived polymer a weak peak at  $\approx 45$  ppm is observed; this peak is much intense in the Mo derived polymer. The DEPT spectra (not shown) indicates that this peak is associated with a methine carbon, and its chemical shift corresponds to the position of the *trans* allylic carbon signal in other fluorinated polynorbornenes. The *cis* allylic carbon signal would be expected at  $\sim 40$  ppm; signals at this position are seen in both spectra, although there is considerable overlap of resonances in this region. This observation would tend to suggest that the Re based polymer has a high *cis* vinylene content and the Mo derived polymer has a high *trans* double bond content. By comparing the intensity of the signal at 45 ppm in the Ru and W initiated polymers, it can be determined that the Ru derived polymer has a *trans* vinylene content, of similar order to the Mo derived polymer, and the W initiated polymer has a lower *trans* content. No further structurally useful information could be obtained from these spectra.

Thus, it can be postulated that the *trans* vinylene content of samples of poly(5-pentafluorophenylnorbornene) increases in the order  $\text{Ru} > \text{Mo} > \text{W} > \text{Re}$ . However, the analysis must be treated with caution, since the resolution, and signal to noise ratio of the spectra are not good, and overlap of signals makes interpretation difficult. Also, the results are not in full agreement with the information obtained from the infrared spectra. Nevertheless, the *cis/trans* vinylene content of

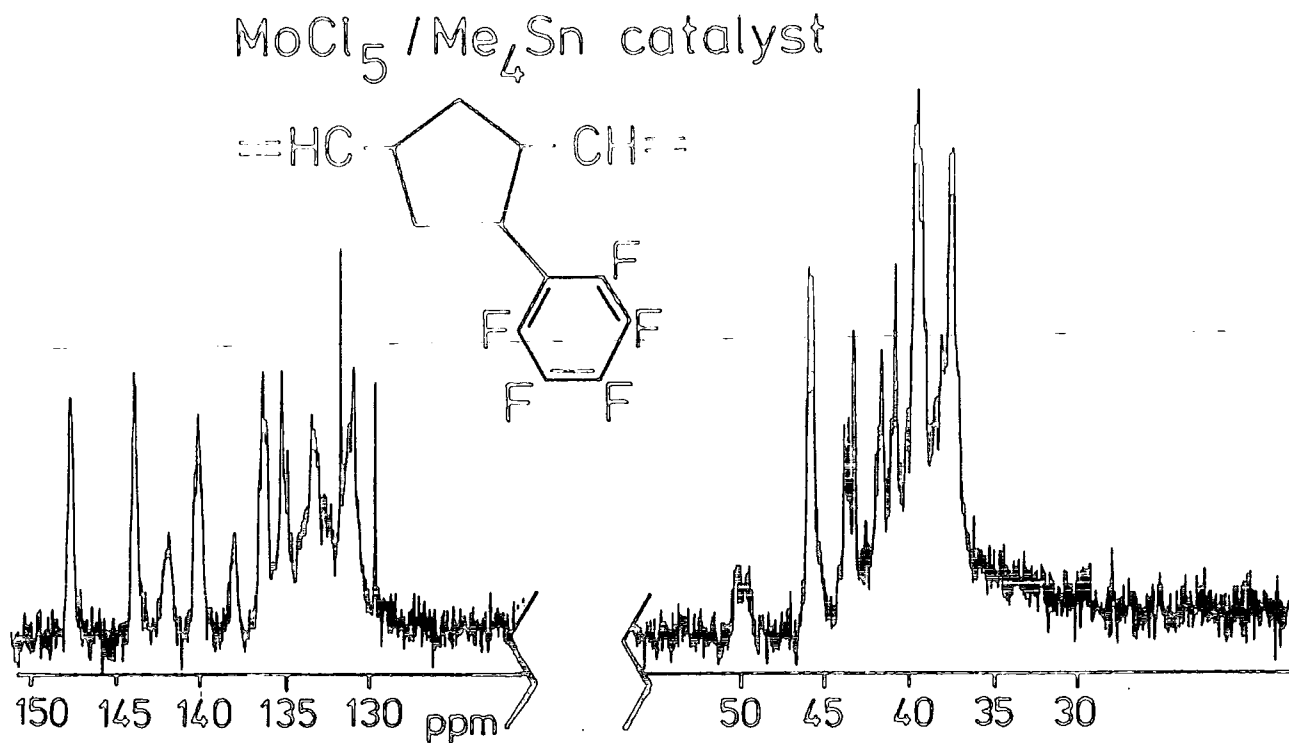


FIGURE 4.7  $^{13}\text{C}$  N.m.r. spectrum of poly(5-pentafluorophenylnorbornene) prepared *via*  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  initiation

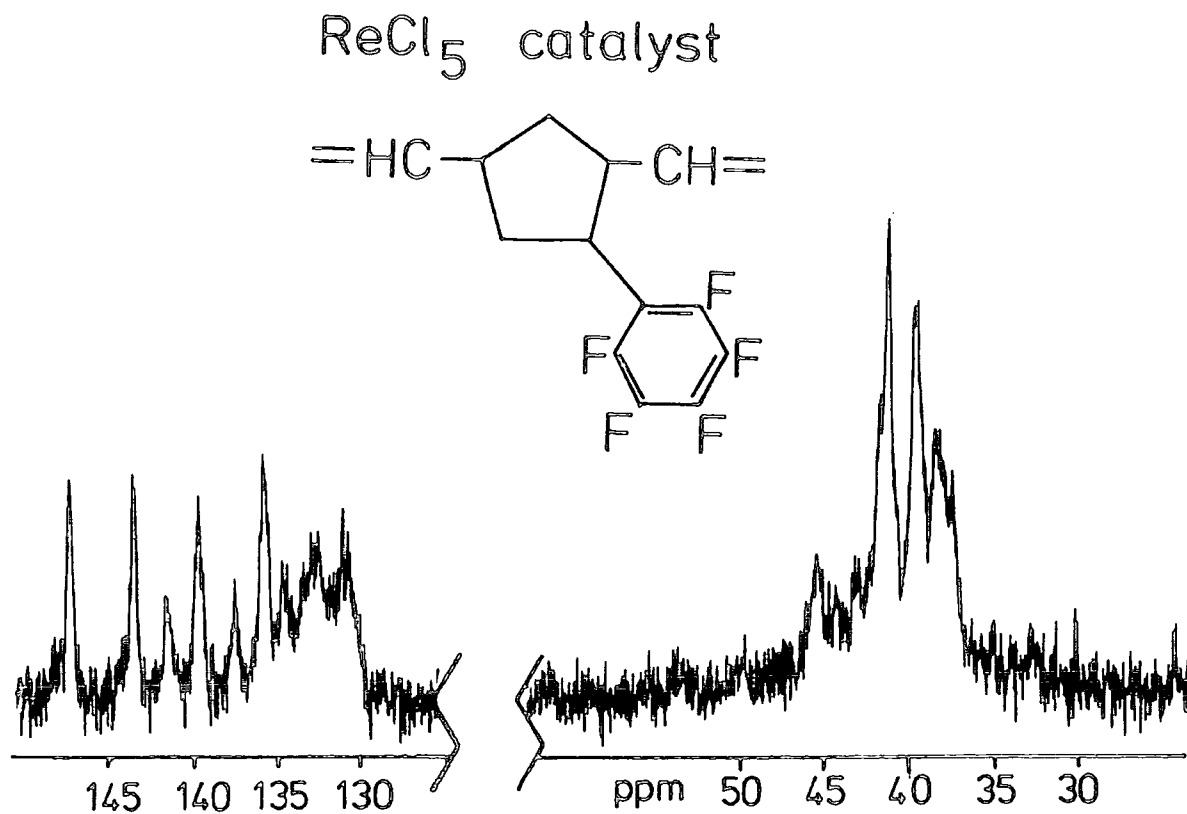


FIGURE 4.8  $^{13}\text{C}$  N.m.r. spectrum of poly(5-pentafluorophenylnorbornene) prepared *via*  $\text{ReCl}_5$  initiation

the polymers prepared from different catalysts appears to follow the trend observed for other fluorinated poly(norbornenes).

#### 4.4 Polymerization of exo(VII) and endo(VIII)-pentafluorophenyl-2,3-dicarboximidenorbornene

##### (a) General

Calderon and Castner<sup>77</sup> observed that pure endo-5-norbornene-2,3-dicarboxyanhydride was relatively inert to metathesis polymerization, whereas the exo isomer readily polymerized. The same authors also found that when a mixture of exo and endo isomers was polymerized, the conversion was dependent upon the amount of exo isomer present. The unpolymerized monomer was recovered which clearly indicated that the exo isomer had been preferentially polymerized, but some endo monomer had also been incorporated. They concluded from their experiments that the barrier to endo/endo linking was either in the carbene to metallocycle transition state, or due to steric restrictions in the polymer chain itself. Exo and endo-N-pentafluorophenyl-2,3-dicarboximide norbornene were exposed to metathesis catalysts, as detailed in Table 4.3.

The exo isomer was readily polymerized using W and Mo based catalysts. However, attempts to polymerize the monomer with  $\text{RuCl}_3$  and  $\text{OsCl}_3$  catalysts proved unsuccessful. The endo isomer could not be polymerized *via*  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  or  $\text{WCl}_6/\text{Me}_4\text{Sn}$  catalysis, in any of several attempts. A mixture of exo and endo isomers was polymerized using  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  as catalyst, giving a relatively low yield of polymer. These results are analogous to those obtained by Calderon and Castner.

TABLE 4.3 Polymerization of exo and endo-N-pentafluorophenyl-2,3-dicarboximide norbornene

Monomer (mmole)	Catalyst (mmoles)	Cocatalyst (mmole)	Solvent <sup>a</sup> (cm <sup>3</sup> )	Temp <sup>b</sup> (°C)	Time (hrs)	Yield <sup>c</sup> (%)
exo (10.58)	WCl <sub>6</sub> (0.071)	Me <sub>4</sub> Sn (0.142)	C, (20.8)	RT	24	45
exo (5.56)	MoCl <sub>5</sub> (0.034)	Me <sub>4</sub> Sn (0.068)	C, (11.4)	60	0.75	89
exo (1.9 + endo 1.9)	MoCl <sub>5</sub> (0.038)	Me <sub>4</sub> Sn (0.076)	C, (12)	60	1.75	39
endo (4.04)	MoCl <sub>5</sub> (0.080)	Me <sub>4</sub> Sn (0.160)	C, (11.1)	60	24	-
endo (6.14)	WCl <sub>6</sub> (0.041)	Me <sub>4</sub> Sn (0.084)	C, (15)	60	36	-

- a. C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.
- b. Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.
- c. After reprecipitation and drying under vacuum for at least 24 hours.

(b) Infrared spectra of polymers of N-pentafluorophenyl-2,3-dicarboximide norbornene

The infrared spectra of the polymers of N-pentafluorophenyl-2,3-dicarboximide norbornene are shown in Figure 4.9. No structurally useful information could be obtained from these spectra, other than to confirm the presence of expected functional groups. In particular, the C-H out of plane bending region for the *cis* and *trans* vinylenes did not yield any information due to the overlap of other absorbances.

(c) <sup>13</sup>C N.m.r. spectra of polymers of N-pentafluorophenyl-2,3-dicarboximide norbornene

The spectrum of the polymer obtained *via* MoCl<sub>5</sub> catalysis is shown in Figure 4.10, and the chemical shifts and assignments recorded in Table 4.4. The repeat unit of the polymer and the numbering system used when assigning spectra is shown in Figure 4.11.

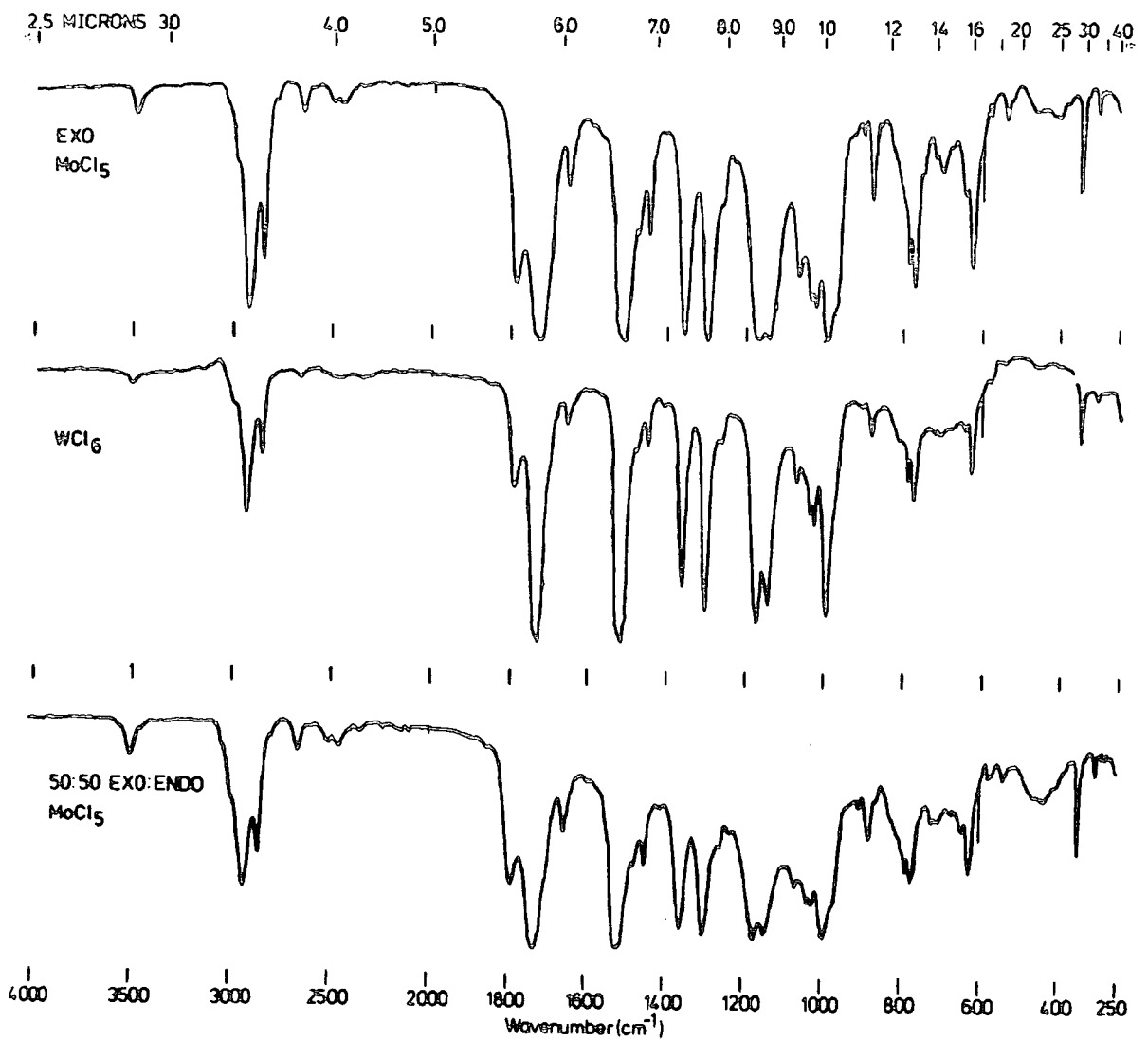


FIGURE 4.9 Infrared spectra of samples of poly(N-pentafluorophenyl-2,3-dicarboximidenorbornene)

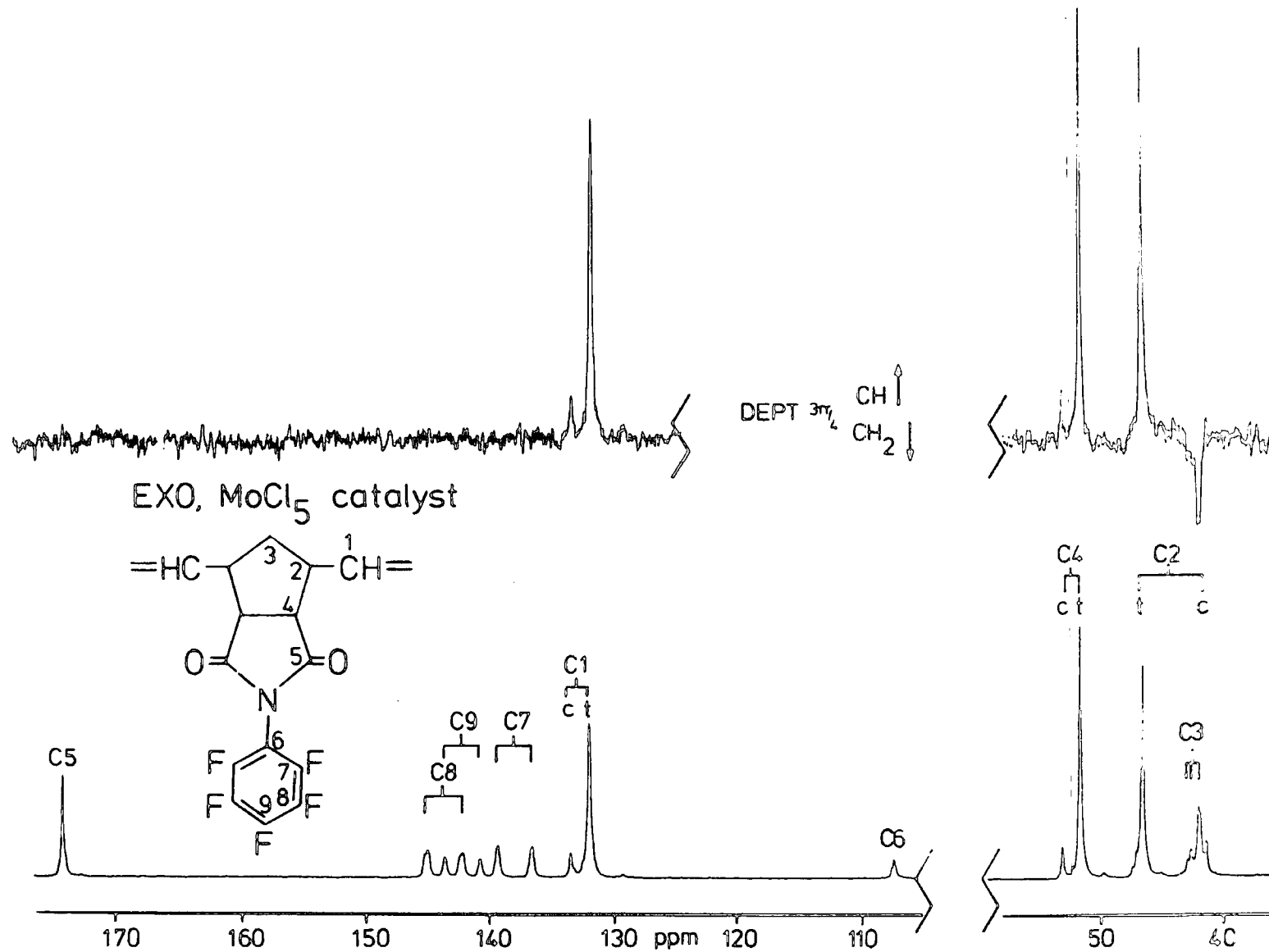


FIGURE 4.10 <sup>13</sup>C N.m.r. spectrum of poly(exo-N-pentafluorophenyl-2,3-dicarboximidenorbornene) prepared via MoCl<sub>5</sub>/Me<sub>4</sub>Sn initiation

TABLE 4.4  $^{13}\text{C}$  N.m.r. chemical shifts and assignments of samples of poly(N-pentafluorophenyl-2,3-dicarboximide norbornene)

Catalyst			Assignment
Exo, $\text{MoCl}_5$	Exo, $\text{WCl}_6$	Exo/Endo $\text{MoCl}_5$	
174.62	174.61	174.61	C5 exo
		173.2	C5 endo
143.57, $^1J_{\text{C-F}}=263\text{Hz}$	143.5, $^1J_{\text{C-F}}=251\text{Hz}$	143.4, $^1J_{\text{C-F}}=250\text{Hz}$	C8
142.13, $^1J_{\text{C-F}}=258\text{Hz}$	142.06, $^1J_{\text{C-F}}=255\text{Hz}$	142.1, $^1J_{\text{C-F}}=259\text{Hz}$	C9
137.32, $^1J_{\text{C-F}}=254\text{Hz}$	137.8, $^1J_{\text{C-F}}=253\text{Hz}$	138.0, $^1J_{\text{C-F}}=252\text{Hz}$	C7
133.36	133.30	133.30	C1, <i>cis</i>
	132.35 )		
	)		
131.88	131.81 )	131.86	C1, <i>trans</i>
		131.27	endo
		129.10	endo
107.14	107.10	107.00	C6
	53.02		C4 ct
52.90	52.87	52.89	C4 cc
	52.05		C4 tc
51.41	51.41	51.40	C4 tt
	49.55	49.55	endo
		47.17	endo
46.95	46.95	46.95	)
			)
46.56		46.56	) C2, <i>trans</i>
			)
46.38	46.40	46.38	)
		45.19	endo
		44.87	endo
	42.78		C3, cc
42.47	42.47	42.46	C3, ct≡tc
41.91 )	41.90	41.89	C3, tt
)			
41.78			
41.27	41.33	41.26	C2, <i>cis</i>
	40.63		endo



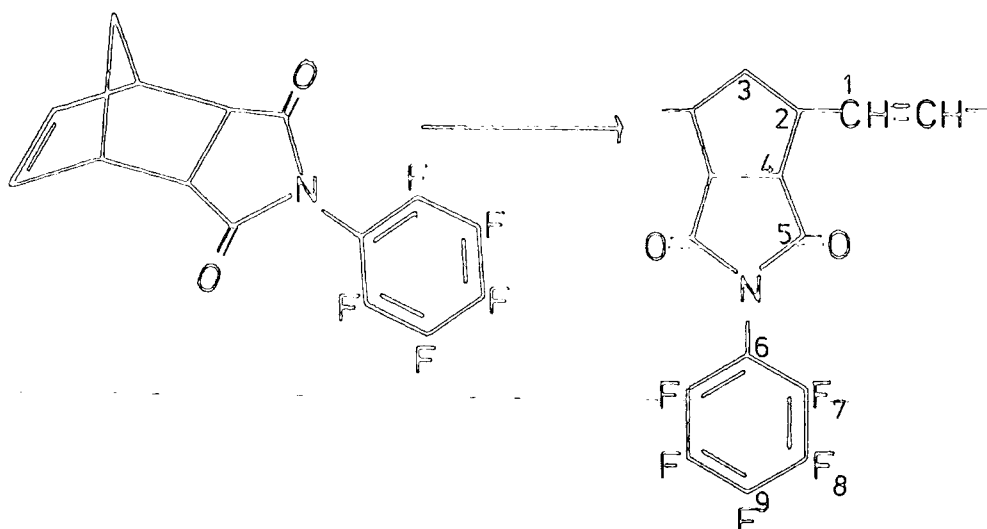


FIGURE 4.11 Ring opening polymerization of N-pentafluorophenyl-2,3-dicarboximide norbornene

The C5 resonance in Figure 4.10 is easily distinguished as the lowest field signal. The carbons of the pentafluorophenyl group are observed as low intensity doublets and are assigned by analogy with related compounds. The C6 resonance appears at  $\approx 107$  ppm, and is absent in the DEPT spectrum. The vinylene carbon signal is resolved into *cis* and *trans* environments as indicated, giving a value of  $\sigma_C$  of 0.09. At high field the C4 *cis* and *trans* environments are assigned to the signals at 52.90 and 51.41 ppm respectively. A low intensity peak, observed adjacent to the *trans* signal may be a tc or ct resonance. These signals give  $\sigma_C$  value of 0.09. The *trans* allylic carbon signal is observed at 46.56 ppm, and consideration of the expected 5 ppm upfield shift of the *cis* environment, allows the C2 *cis* signal to be assigned to the peak at 41.27 ppm; this signal overlaps with the methylene carbon signals, but the DEPT spectrum confirms the assignment.

The *trans* signal appears to be resolved into two peaks, with a low intensity shoulder. The signals may be a consequence of the resolution of the *tt* and *tc* environments and/or *m/r* effects. The  $\sigma_c$  value for this carbon is 0.12. The C3 resonance is resolved into 3 peaks assigned to the *cc*, *tc=ct* and *tt* environments. The *cc* peak was not detected by the computer and the integral for this peak was estimated; the value of  $\sigma_c$  from this carbon is 0.15. The *tt* peak is resolved into two signals of approximately equal intensity, which could be a result of *m/r* splitting, and indicates that the polymer is atactic.

The overall conclusion from this analysis is that the polymer has a high *trans* vinylene content. The values of  $\sigma_c$  calculated from the C3 and C2 signals are not very reliable since the peaks overlap, and consequently the integrals are inaccurate. However, all  $\sigma_c$  values indicate a high *trans* double bond content, and the resolution of the C3 resonance suggests the polymer is probably atactic.

Figure 4.12 shows the spectrum of the polymer derived *via*  $WCl_6$  initiation. The C5, C6, C7, C8 and C9 resonances are assigned by analogy with the  $MoCl_5$  derived polymer. The C1 resonance is again resolved into *cis* and *trans* environments, and the *trans* signal is observed as two peaks, a consequence of *cis/trans* vinylene effects or *m/r* splitting. The vinylene signals give a value of  $\sigma_c$  of 0.36. The C4 resonance appears as four signals assigned to the *cc*, *ct*, *tc*, and *tt* environments of this carbon; a value of  $\sigma_c = 0.39$  is obtained. Carbons C2 and C3 are assigned by comparison with the spectrum of the polymer derived from  $MoCl_5$  catalysis, and

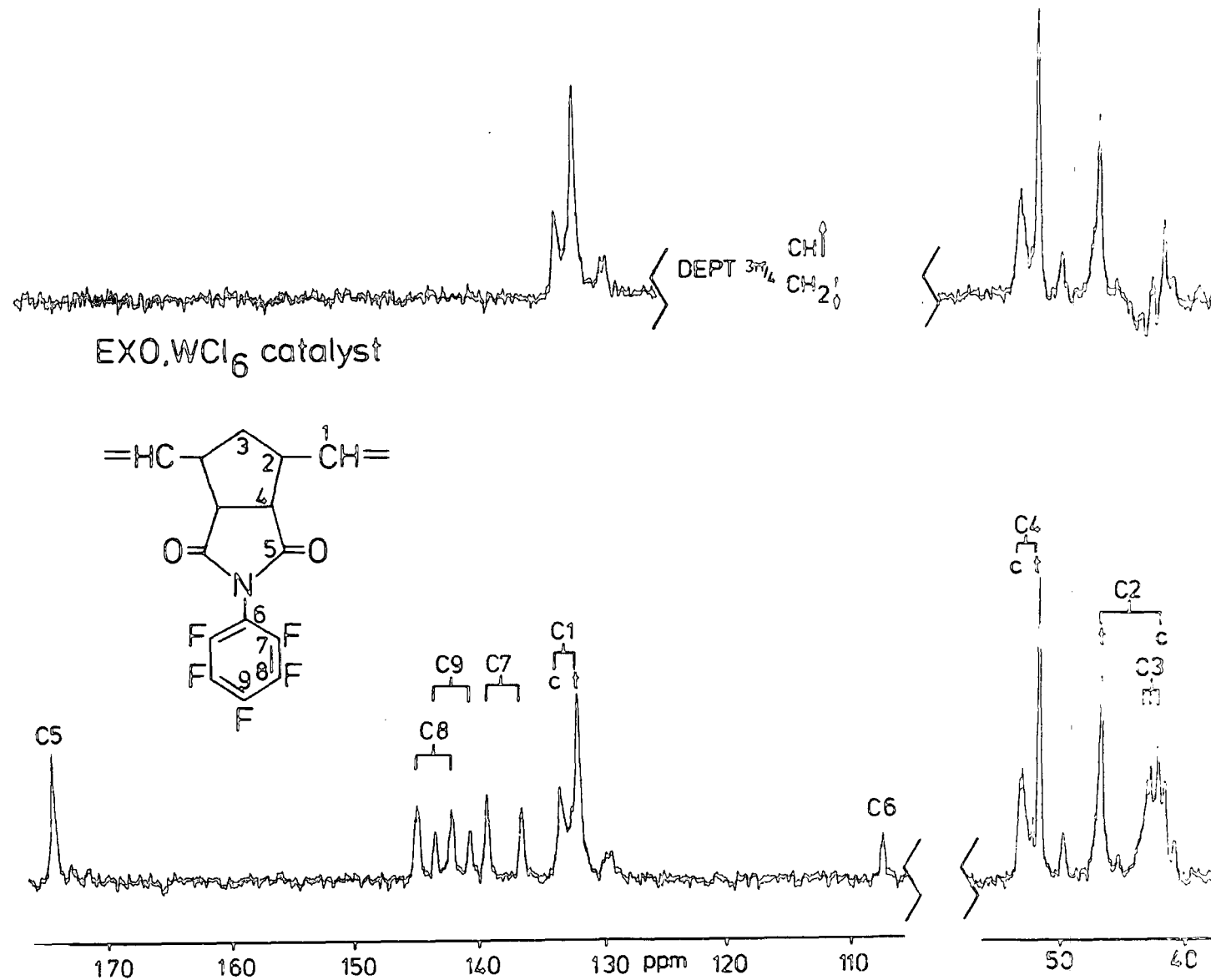


FIGURE 4.12 <sup>13</sup>C N.m.r. spectrum of poly(exo-N-pentafluorophenyl-2,3-dicarboximidenorbomene) prepared via WCl<sub>6</sub>/Me<sub>4</sub>Sn initiation

give  $\sigma_C$  values of 0.23 and 0.49 respectively. There seems to be some discrepancies in the  $\sigma_C$  values; overlap of the C2 and C3 carbon signals makes the integrals and hence,  $\sigma_C$  values for these carbon unreliable. The C1 and C4 signals are well resolved, and the values of  $\sigma_C$  calculated from these carbon signals are in reasonable agreement. Hence, it can be concluded that the polymer has a mixture of *cis* and *trans* vinylenes. Broadening and the occurrence of fine structure for most of these signals probably implies that the polymer is atactic.

The  $^{13}\text{C}$  n.m.r. of the polymer produced from polymerizing a mixture of *exo* and *endo* isomers *via*  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  initiation is shown in Figure 4.13. The shifts and assignments are recorded in Table 4.4. The spectrum is very similar to that obtained from polymerization of the *exo* isomer using  $\text{MoCl}_5$  as catalyst, except some of the weak peaks have increased in intensity. These peaks can be confidently assigned to carbons associated with *endo* units, and by comparison of the integral of the *exo* and *endo* signals, it is apparent that the *exo* isomer has been preferentially incorporated into the polymer chain. The signals of the carbons derived from *endo* isomer are marked (e) on the spectrum and those associated with the *exo* isomer are assigned by analogy with the previous spectra. The  $\sigma_C$  values were 0.17 for the vinylene carbons, 0.23 for C4, 0.17 for C2, and 0.23 for C3. The overlap of signals with *endo* carbon resonances makes the reliability of the values uncertain, but it is apparent that the vinylenes adjacent to *exo* units have a high *cis* stereochemistry.

Thus, the conclusion to be drawn from analysis of the spectra is that the  $\text{MoCl}_5$  based catalysts give a high *trans*

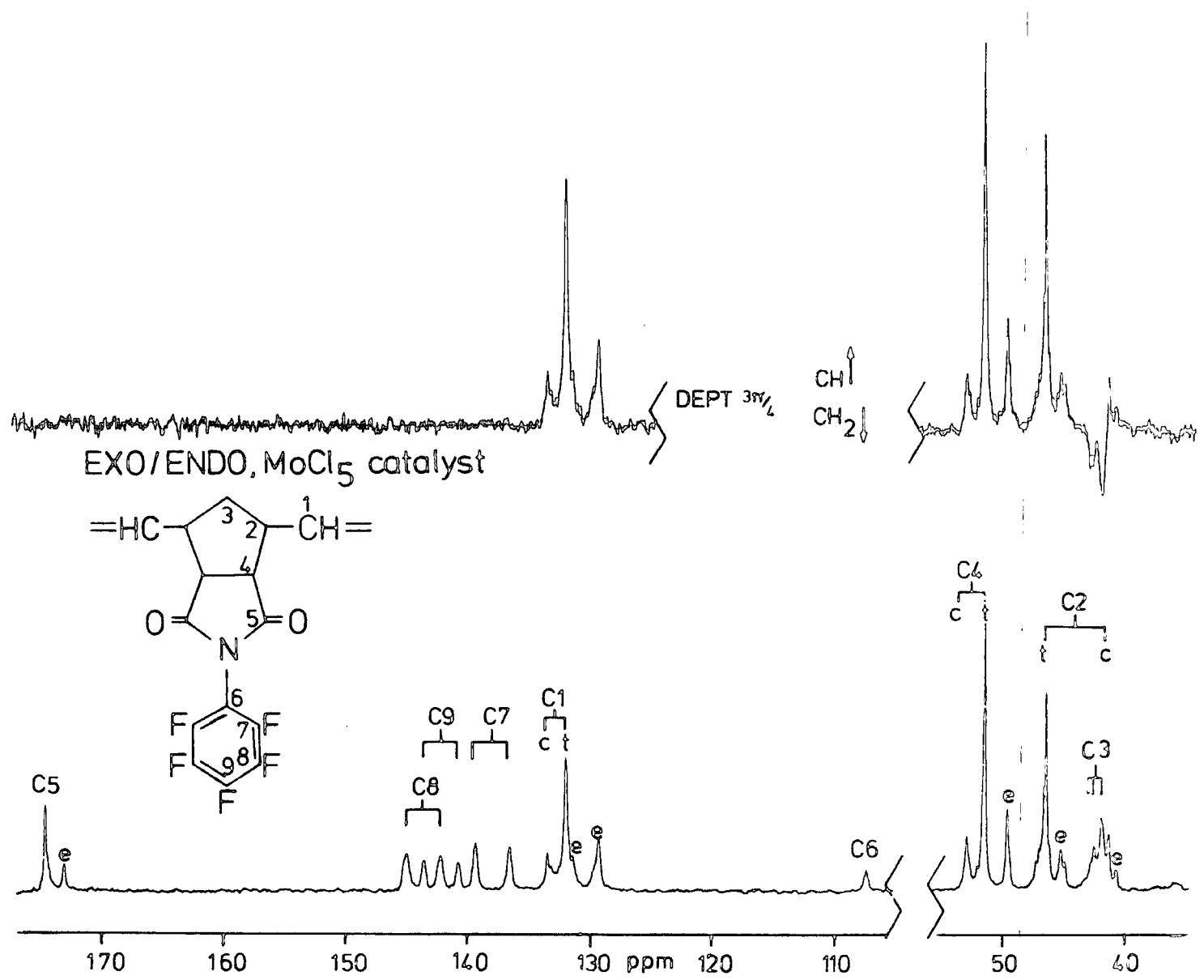


FIGURE 4.13  $^{13}\text{C}$  N.m.r. spectrum of the polymer produced from  $\text{MoCl}_5$  initiation of an exo/endo mixture of N-pentafluorophenyl-2,3-dicarboximidenoborene

vinylene content, and  $WCl_6$  based polymers give a mixture of *cis* and *trans* double bonds. The polymerization of a mixture of exo and endo isomers shows that exo monomer is preferentially incorporated into the chain.

#### 4.5 Polymerization of 5-perfluorohexylnorbornene(IX)

5-Perfluorohexylnorbornene was polymerized with a range of metathesis catalysts, as detailed in Table 4.5.

TABLE 4.5 Polymerization of 5-perfluorohexylnorbornene

Monomer (mmole)	Catalyst (mmoles)	Cocatalyst (mmole)	Solvent <sup>a</sup> (cm <sup>3</sup> )	Temp <sup>b</sup> (°C)	Time (hrs)	Yield <sup>c</sup> (%)
8.52	$WCl_6$ (0.042)	$Me_4Sn$ (0.084)	C, 1.7	RT	2 min	76
5.27	$MoCl_5$ (0.026)	$Me_4Sn$ (0.052)	C, 0.7	RT	2 min	53
4.95	$OsCl_3$ (0.025)	-	CE, 0.7	50	24	39
5.51	$ReCl_5$ (0.027)	-	C, 0.5	50	4	29

- C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.
- Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.
- After reprecipitation and drying under vacuum for at least 24 hours.

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The polymers obtained were all found to be insoluble in a wide range of common organic solvents, even after attempts to reduce the molecular weight using *trans*-4-octene. One solvent, however, methylheptafluorobutyrate was found to slowly dissolve the polymers. The infrared data obtained for the polymers was poorly resolved, and no structurally useful information could be derived from them. <sup>13</sup>C N.m.r. spectra would be expected to be complex for a monomer which was unsymmetrical,

and a mixture of exo and endo isomers. In addition, the long perfluoroalkyl chain increases the number of carbon resonances, and reduced the solubility of the polymers. Although they were all soluble in methyl heptafluorobutyrate only dilute solutions could be obtained and it proved impracticable to record useful n.m.r. spectra. Nevertheless, it has been demonstrated that long perfluoroalkyl substituents can be tolerated by metathesis catalysts. It is also noteworthy that the polymerization using  $\text{ReCl}_5$  as initiator occurs reasonably rapidly, and in fairly good yield for this catalyst.

#### 4.6 Polymerization of 5-perfluorooctylnorbornene(X)

The details of the polymerization of 5-perfluorooctylnorbornene with a range of metathesis catalyst are given in Table 4.6.

TABLE 4.6 Polymerization of 5-perfluorooctylnorbornene

Monomer (mmole)	Catalyst (mmoles)	Cocatalyst (mmole)	Solvent <sup>a</sup> (cm <sup>3</sup> )	Temp <sup>b</sup> (°C)	Time (hrs)	Yield <sup>c</sup> (%)
3.41	$\text{WCl}_6$ (0.017)	$\text{Me}_4\text{Sn}$ (0.034)	0.7	RT	2 min	57
3.91	$\text{MoCl}_5$ (0.020)	$\text{Me}_4\text{Sn}$ (0.040)	0.5	RT	2 min	90
2.54	$\text{RuCl}_3$ (0.013)	-	0.3	60	24	33
4.07	$\text{ReCl}_5$ (0.020)	-	0.4	50	24	22

- C - chlorobenzene, CE - 1:1 (vol for vol) mixture of chlorobenzene and ethanol.
- Approximate temperature. Some polymerizations were notably exothermic, no monitor of temperature was placed in the vessel.
- After reprecipitation and drying under vacuum for at least 24 hours.

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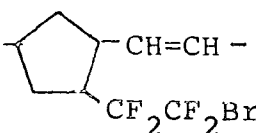
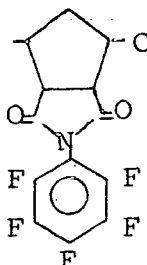
Again, the polymers were found to be insoluble in common organic solvents, but were sparingly soluble in methyl heptafluorobutyrate. Infrared and  $^{13}\text{C}$  n.m.r. spectroscopic data for the polymers were not of sufficiently good quality to be interpreted in terms of polymer chain microstructures but were consistent with the assigned structure.

#### 4.7 Gel permeation chromatography and molecular weight distribution

Gel permeation chromatography has been used as a rapid and efficient method of determining molecular weight of polymers.<sup>159-161</sup> Molecular size separation is achieved by injecting a solution of the polymer onto a column consisting of a crosslinked polystyrene gel. Molecules which are larger than the pore size of the gel pass through, whereas smaller molecules enter the pores. Hence, small molecules have longer retention times. The gel permeation curve, obtained by measuring the refractive index of the eluted material, reflects the polymers molecular weight distribution; larger molecules are represented at the front of the curve. The conversion of the elution volume to a number average and weight average molecular weight has been described previously.<sup>89</sup> Polymer samples were dissolved in tetrahydrofuran to give a 0.5% solution, and filtered through 10 $\mu\text{m}$  and 0.5 $\mu\text{m}$  millipore filters, and injected onto the column. The weight average and number average molecular weights, together with the values of polydispersity, of the polymers which were soluble in tetrahydrofuran are recorded in Table 4.7.



TABLE 4.7 Molecular weights of polymers of (V) and (VII)

Polymer	Catalyst	$\bar{M}_n (10^5)$	$\bar{M}_w (10^5)$	Poly-dispersity
	WCl <sub>6</sub> /Me <sub>4</sub> Sn	0.33	0.95	2.58
	MoCl <sub>5</sub> /Me <sub>4</sub> Sn	0.58	2.50	2.32
	RuCl <sub>3</sub> /Me <sub>4</sub> Sn	0.60	1.30	2.16
	ReCl <sub>5</sub> /Me <sub>4</sub> Sn	0.83	2.00	2.41
	exo, WCl <sub>6</sub> /Me <sub>4</sub> Sn	1.99	8.80	4.42
	exo, MoCl <sub>5</sub> /Me <sub>4</sub> Sn	3.05	12.60	4.13
	endo + exo, MoCl <sub>5</sub>	1.05	3.50	3.33

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The results show that the materials produced are genuine high polymers, and that the polymers have a fairly wide range of molecular weights.

#### 4.8 Conclusions

A range of fluorinated norbornene derivatives, substituted in the 5- and 6-position can be tolerated by metathesis catalysts. Inspection of the <sup>13</sup>C n.m.r. spectra of the polymers confirms the general trends determined for the simpler fluorinated norbornenes and norbornadienes; Os, Ru, and Mo based catalysts give rise to polymers with high *trans* vinylene contents, whereas ReCl<sub>5</sub> gives polymers with a high *cis* double bond content, and W based catalysts have the lowest tendency to produce regular structures.

EXPERIMENTAL

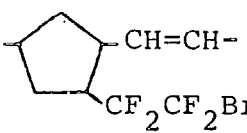
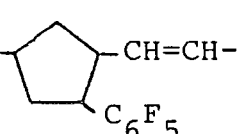
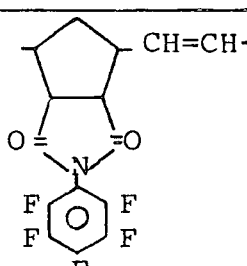
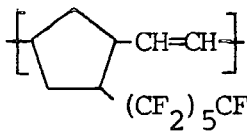
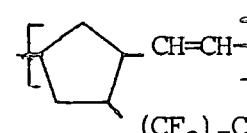
4.9 Reagents

Reagents and suppliers are as detailed in Chapter Three.

4.10 Polymerization procedure

The method of polymerization was as described in Chapter Three. Details of the reaction conditions, and catalyst and monomer concentrations are given in the script. The polymers produced were purified by successive reprecipitation, and the solvents and non-solvents are recorded in Table 4.8.

TABLE 4.8 Non-solvents and solvents for some fluorinated polynorbornenes

Polymer	Catalyst	Solvent	Non-solvent
	$WCl_6/Me_4Sn$ $MoCl_5/Me_4Sn$ $RuCl_3/Me_4Sn$ $ReCl_5/Me_4Sn$	acetone	methanol
	$WCl_6/Me_4Sn$ $MoCl_5/Me_4Sn$ $RuCl_3/Me_4Sn$ $ReCl_5/Me_4Sn$	chloroform	methanol
	Exo, $WCl_6/Me_4Sn$ Exo, $MoCl_5/Me_4Sn$ Endo, + Exo, $MoCl_5/Me_4Sn$	butanone	methanol
	$WCl_6/Me_4Sn$ $MoCl_5/Me_4Sn$ $OsCl_3$ $ReCl_5$	methyl heptafluorobutyrate	hexane
	$WCl_6/Me_4Sn$ $MoCl_5/Me_4Sn$ $OsCl_3$ $ReCl_5$	methyl heptafluorobutyrate	hexane

CHAPTER FIVE

PHYSICAL PROPERTIES OF SOME FLUORINATED  
POLY (NORBORNENES) AND POLY (NORBORNADIENES)

## 5.1 Introduction

This chapter is concerned with an investigation into some of the physical properties of polymers produced during the course of this work. Generally, the polymerizations were carried out on a small scale, and hence these investigations of physical properties were only carried out with the more readily available polymers. The thermal behaviour of the polymers was investigated using differential scanning calorimetry and thermogravimetric analysis. A knowledge of the thermal behaviour of a polymer is required to determine the limits of its working range, and hence the limits on its potential end uses.

An attempt to investigate the potential piezoelectric behaviour of one of the polymers was unsuccessful.

## 5.2 Differential Scanning Calorimetry

Differential scanning calorimetry is a well established technique for investigating chemical reactions and physical changes which involve a flow of heat into or out of a sample. In polymer science it has been widely used in studies of the glass transition phenomena, melting, cure, and degradation processes. Many polymers exhibit some degree of crystallinity and crystalline regions are most easily formed from regular chains. Hence, polymers which are stereoregular might be expected to be crystalline, and display a crystalline melting point ( $T_m$ ), although this is not absolutely essential. Amorphous regions of polymers (in which the polymer chains are arranged in a random fashion), when heated, will undergo a

glass transition ( $T_g$ ), during which the chain mobility undergoes a large increase in a small temperature interval. The polymer changes from a rigid, glassy solid to a rubberlike material as it passes through the glass transition temperature.

Many polymer samples contain varying proportions of ordered and disordered regions. These semicrystalline polymers usually exhibit both a glass transition temperature and a crystalline melting point.

Differential scanning calorimetry detects the enthalpy changes occurring at  $T_g$  or  $T_m$ . With the instrument used in this work, a Perkin-Elmer D.S.C.II, a sample of the polymer (typically 10mg) was placed in an aluminium sample pan, and an empty pan used as a reference. The pans were placed in cells in a heating block, and heated at a uniform rate (10K/min). The energy input to the sample or reference from the cells was maintained so both sample and reference remained at the same temperature. The output obtained represented the amount of electrical energy supplied to the system, and the areas under the peaks was proportional to the change in enthalpy which occurred.

The glass transition temperature is observed as a deflection in the base line. The  $T_g$  was calculated from the output as the temperature at which the change in heat capacity was half the maximum as shown in Figure 5.1.

Table 5.1 lists the glass transition temperatures of some of the polymers prepared in this work.

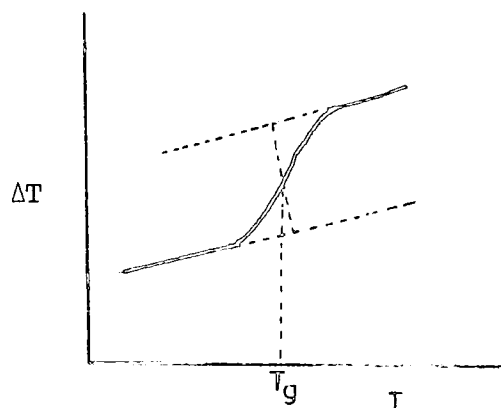
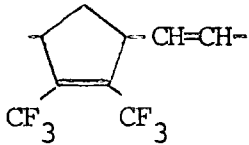
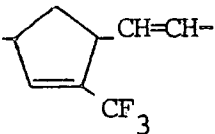
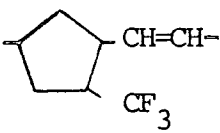
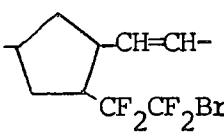
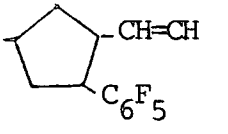


FIGURE 5.1

TABLE 5.1 Glass transition and decomposition temperatures of some fluorinated poly(norbornenes) and poly(norbornadienes)

Polymer	Catalyst	Micro-structure (from $^{13}\text{C}$ n.m.r.)	$T_g$ (K)	Decomposition (K)
	$\text{MoCl}_5/\text{Me}_4\text{Sn}$ (RT)	high <i>trans</i>		405
	$\text{MoCl}_5/\text{Me}_4\text{Sn}$ ( $-20^\circ\text{C}$ )	?		438
	$\text{WCl}_6/\text{Me}_4\text{Sn}$	<i>cis/trans</i>	398	
	$\text{RuCl}_3$	high <i>trans</i>	390	
	$\text{MoCl}_5/\text{Me}_4\text{Sn}$	high <i>trans</i>	358	405
	$\text{WCl}_6/\text{Me}_4\text{Sn}$	<i>cis/trans</i>		403
	$\text{OsCl}_3$	<i>cis/trans</i>		402
	$\text{OsCl}_3$ (exo)	all <i>trans</i>	355	
	$\text{OsCl}_3$ (endo)	high <i>trans</i>	344	
	$\text{MoCl}_5/\text{Me}_4\text{Sn}$ (endo)	high <i>trans</i>	355	
	$\text{ReCl}_5$ (endo)	all <i>cis</i> , stereoregular	345	
	$\text{MoCl}_5/\text{Me}_4\text{Sn}$	high <i>trans</i>	349	
	$\text{WCl}_6/\text{Me}_4\text{Sn}$	<i>cis/trans</i>	370	
	$\text{ReCl}_5$	all <i>cis</i>	360	
	$\text{WCl}_6/\text{Me}_4\text{Sn}$	<i>cis/trans</i>	373	
	$\text{ReCl}_5$	high <i>cis</i>	341	501

The samples were heated from 300K at  $10\text{K min}^{-1}$  until a transition was observed, then cooled at  $320\text{K/min}$ , and the procedure repeated. The values of  $T_g$  (when detected) and decomposition temperatures recorded in Table 5.1 represent the average values obtained from a number of experiments. A crystalline melting point was not detected for any of the polymers, even when samples heated above their glass transition temperature were annealed slowly at  $1\text{K/min}$ . This result is disappointing in view of the fact that some of the polymers are believed to be stereoregular, but this does not exclude stereoregularity. For some polymers neither a crystalline melting point, nor a glass transition temperature could be detected, and an exothermic peak believed to correspond to decomposition was observed. On opening the cooled sample pan after detection of this peak, black, charred material was invariably obtained.

On inspection of the data acquired for specific polymers it can be seen that for poly(2,3-bis(trifluoromethyl)-norbornadiene) derived from  $\text{MoCl}_5$  catalysis only a decomposition peak was observed, whereas for the W and Ru derived polymers, both of which were concluded to be atactic from  $^{13}\text{C}$  n.m.r. analyses, gave similar values of  $T_g$  and no exothermic decomposition peak below 530K. The  $^{13}\text{C}$  n.m.r. analysis suggests that both the Mo and Ru derived samples were high *trans* and atactic, and the marked difference in their thermal behaviour is puzzling.

The polymers of 2-trifluoromethylnorbornadiene all gave decomposition temperatures in a similar range; in this case a glass transition temperature was detected for the Mo derived



polymer only. Again this is surprising since the Os and Mo derived samples have similar microstructures according to the  $^{13}\text{C}$  n.m.r. analysis. These differences between superficially similar samples indicate that there must be factors other than polymer microstructure which are important in determining thermal behaviour. The most likely causes of these discrepancies would appear to be differences in molecular weight distribution or the presence of trace impurities derived from catalyst residues.

Comparison of the glass transition temperatures obtained for samples of poly(2-trifluoromethylnorbornadiene) and poly(2,3-bis(trifluoromethyl)-norbornadiene) is consistent with the theory that, for polymers with stiff backbones the nature of the side groups is important in determining the glass transition temperature; the bulkier the side group the higher the value of  $T_g$  observed. This effect is a result of the restriction on molecular motion caused by bulky substituents; consequently the polymer must be heated to a higher temperature to permit chain movement.<sup>162,163</sup> Two trifluoromethyl substituents on a cyclopentene ring seem to cause more restriction on motion than one  $\text{CF}_3$  group. This observation supports the argument presented earlier (Chapter Three), in which it was postulated that for polymers of 2-trifluoromethylnorbornadiene *cis* head-head junctions were formed more easily than in the 2,3-bis(trifluoromethyl)norbornadiene case, because rotation of the bonds around the allylic carbons allows the trifluoromethyl groups to adopt a reasonably sterically favoured configuration which is forbidden for the more substituted system. These factors are reflected in the glass transition temperature.

The glass transition temperatures obtained for polymers of 5-trifluoromethylnorbornene are perhaps the most interesting since it was for these polymers that the microstructures were most confidently assigned. The polymer obtained from  $\text{OsCl}_3$  catalysis of the exo isomer gave a  $T_g$  very similar to the polymer of 2-trifluoromethylnorbornadiene obtained from  $\text{MoCl}_5$  catalysis. Both polymers were concluded to have high *trans* atactic stereochemistries, and the steric restrictions on motion of the two polymers are probably similar. It is, therefore, not surprising that both give very similar glass transition temperatures.

The polymers derived from the endo isomer of 5-trifluoromethylnorbornene all gave very similar  $T_g$  values. The tacticities of these polymers were concluded to be all *cis* and stereoregular for the  $\text{ReCl}_5$  derived polymer, and high *trans* and atactic for the  $\text{OsCl}_3$  and  $\text{MoCl}_5$  derived polymers. Tacticity effects in polymer chains can, in some cases, have dramatic effects on the glass transition temperature. Hence, for poly(methylmethacrylate) the syndiotactic, isotactic and atactic microstructures gave glass transition temperatures of 115, 45 and  $105^\circ\text{C}$  respectively. It was concluded that the variation in the value of  $T_g$  for the different tacticities of polymers, which were otherwise chemically identical, was a consequence of the relative placement of substituents, and the resultant interactions between them. In contrast, for poly(acrylates), in which a methyl group has been replaced by a hydrogen, much smaller differences in the values of the glass transition temperatures resulted from a change in tacticity.<sup>164,165</sup> This effect was a result of the reduced steric bulk of the substituent. In this case the introduction of a single trifluoromethyl

group at 5-position in poly(norbornene) raises the glass transition temperature from 308K to 350±5K irrespective of the disposition of the substituent. This is somewhat surprising but indicates that the polymer backbone has a bigger influence than a single trifluoromethyl substituent. The overall results seem self consistent; thus polymers with a single trifluoromethyl substituent on the repeat unit have very similar glass transition temperatures, which are about 40K higher than the hydrocarbon analogue, whereas two trifluoromethyl groups cause a further elevation of about 40K. In general, the polymers of 5-bromo-tetrafluoroethylnorbornene and 5-pentafluorophenylnorbornene, gave higher glass transition temperatures than the other polymers. This result is probably a consequence of the bulky nature of the substituents.

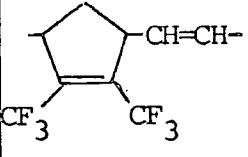
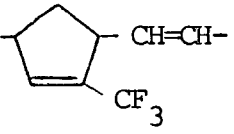
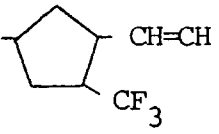
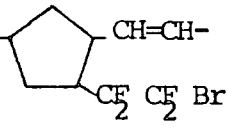
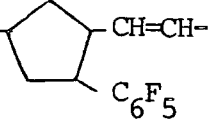
It must be remembered that the glass transition temperature is a function of the molecular weight of the polymer.<sup>166,167</sup> At high masses  $T_g$  is essentially constant, but as the molecular weight is lowered, the glass transition temperature is reduced. The point at which the  $T_g$  is independent of the molecular weight is characteristic for each polymer. The investigation has not been thorough enough to determine if such an effect is influencing the glass transition temperatures observed.

### 5.3 Thermogravimetric Analysis

The thermal stability of polymers can be routinely compared by thermogravimetric analysis. This technique involves measuring the weight loss of a polymer either, as the temperature is increased at a constant rate, or at a constant temperature; however, there does not seem to be a universally

accepted standard procedure to adopt. A Stanton Redcroft TG 760 thermobalance, operating in the percentage weight loss mode was used in this work. A sample of the polymer (<10mg) was placed on the balance, and the instrument programmed to heat at a rate of 10°C/minute from ambient temperature to 1000°C. The decomposition temperature, determined from the trace obtained, was taken as the temperature at which 10% weight loss had occurred. The results are recorded in Table 5.2, which in most cases represent the average values obtained from a series of three experiments.

TABLE 5.2 Decomposition temperatures of some fluorinated poly(norbornenes) and poly(norbornadienes)

Polymer	Catalyst	10% decomposition (°C)
	MoCl <sub>5</sub> /Me <sub>4</sub> Sn (RT) MoCl <sub>5</sub> /Me <sub>4</sub> Sn (-20°C) WCl <sub>6</sub> /Me <sub>4</sub> Sn	330 237 300
	MoCl <sub>5</sub> /Me <sub>4</sub> Sn WCl <sub>6</sub> /Me <sub>4</sub> Sn	396 320
	endo, OsCl <sub>3</sub> endo, ReCl <sub>5</sub> endo, MoCl <sub>5</sub> /Me <sub>4</sub> Sn	400 274 380
	MoCl <sub>5</sub> /Me <sub>4</sub> Sn WCl <sub>6</sub> /Me <sub>4</sub> Sn ReCl <sub>5</sub> /Me <sub>4</sub> Sn	401 388 395
	exo, MoCl <sub>5</sub> exo/endo MoCl <sub>5</sub>	392 355

A general trend, which would allow a physical property/structure correlation to be constructed was not observed. Indeed, if the decomposition temperatures collected in Table 5.2 are compared with those obtained *via* differential scanning calorimetry, then large differences are observed. Even if the actual decomposition temperatures obtained from the two methods differed, the relative order they are observed for polymers within the same group (*i.e.* polymers with the same repeat unit but with different microstructures) might be expected to be the same, and this is not the case. The decomposition temperature of a polymer determined *via* thermal analysis is highly dependent on heating rate and on the type of atmosphere, *e.g.* air, N<sub>2</sub>, helium, employed. In addition, the physical form of the polymer when placed on the thermobalance is also important, since granules, powders or solid blocks of polymer have very different surface areas and will decompose at different rates. The decomposition temperatures recorded in Table 5.2 are recorded under standard conditions, heat rate 10°C/min under N<sub>2</sub> atmosphere. However, the physical form of the polymer was more difficult to control. In addition, some of the polymers were contaminated with small amounts of catalyst residues, which may affect the observed decomposition temperature. These results have been recorded here for the sake of completion, and can be taken to indicate in a rough manner the thermal stability of this class of polymer, but do not bear a detailed analysis.

#### 5.4 Conclusions

In this study several new fluoropolymers have been produced and characterized with respect to their structures. The thermal behaviour of the polymers seem to show considerable variation. However, a firm correlation of microstructure and physical properties could not be established on the basis of the limited data so far available. Nevertheless, the results are encouraging, and a more detailed investigation of the physical properties seems worthwhile, particularly as a wider range of structures becomes available.

CHAPTER SIX

CONCLUSIONS AND PROPOSALS

FOR FURTHER WORK

### Conclusions and Proposals for further Work

The work described in this thesis clearly illustrates that fluoropolymers are easily accessible *via* the olefin metathesis reaction. In favourable cases, it has proved possible to determine the microstructure of the polymer chains produced using  $^{13}\text{C}$  n.m.r. and infrared spectroscopy. Using these methods, it has been concluded that some of the polymers produced *via*  $\text{ReCl}_5$  catalysis are all *cis* and stereoregular. This catalyst seems to be the most selective of those used, but also the least active. This, in itself is a reasonable observation, since a catalyst which selects the direction of approach of an incoming monomer will certainly polymerize at a slower rate than a catalyst in which approach of the monomer is irrelevant. The catalyst produces polymers in which there is an approximately equal number of HH, HT, TH and TT environments. Presumably, the fluorine substituents of repeat units in the polymer chain which are remote from the active centre, do not influence which enantiomer approaches the catalyst site, although the direction of approach of the monomer is clearly critical; it has been postulated that the formation of all *cis* double bonds and stereoregular polymers requires that the monomer approaches the catalyst site in alternating directions, *i.e.*  $M_L$  and  $M_R$ , and that the configuration of ligands around the metal centre changes between propagation steps.

The catalysts,  $\text{MoCl}_5/\text{Me}_4\text{Sn}$ ,  $\text{RuCl}_3$ ,  $\text{OsCl}_3$  and  $\text{IrCl}_3$  give polymers which have a high *trans* vinylene content, and are atactic, and the polymers produced from  $\text{WCl}_6/\text{Me}_4\text{Sn}$  initiation contain a mixture of *cis* and *trans* double bonds and are also atactic. This is indicative of propagation by an achiral



species, or through a chiral species which rapidly epimerizes between additions.

The investigation of the physical properties of the polymers produced, was not detailed enough to determine any property-structure correlation, and more work is required in this area.

Clearly, many aspects of the work described in this thesis could be expanded. In particular, the preparation of, and analysis by  $^{13}\text{C}$  n.m.r. spectroscopy of hydrogenated derivatives of the polymers prepared would be instructive. Comparison of the  $^{13}\text{C}$  n.m.r. spectrum of the unsaturated polymer and its hydrogenated analogue would allow signals to be assigned with more confidence, and provide unambiguous evidence of the tacticities as isotactic, syndiotactic or atactic. From a mechanistic viewpoint, it would be interesting to prepare and polymerize with a variety of catalysts, fluorinated norbornene derivatives substituted in the 1,2 and 7 positions. The effect of substitution on the tacticity of the polymer obtained could then be monitored *via*  $^{13}\text{C}$  n.m.r. The polymerization of 1-trifluoromethyl norbornene with a variety of catalyst may well yield some interesting results. Ivin reports<sup>65</sup> that polymerization of 1-methylnorbornene with  $\text{ReCl}_5$  catalyst gives an all *cis*, all HT polymer, in which (+) and (-) enantiomers form an alternating sequence. The formation of an all HT structure is rationalised in terms of the steric difficulty of forming a *cis*-1,2-disubstituted metallocyclobutane transition state that would be required to form a *cis*-HH dyad. A trifluoromethyl substituent would exert a greater steric influence than a methyl

group and hence, the polymerization of 1-trifluoromethyl norbornene may give analogous results. Therefore, as well as being interesting mechanistically, such experiments would be expected to yield well defined totally stereoregular polymers.

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APPENDIX A

APPARATUS AND INSTRUMENTS

Infrared spectra were recorded using a Perkin-Elmer 457 grating spectrometer.

Mass spectra were recorded on a VG7070E spectrometer.

Combined gas chromatography/mass spectra were recorded on a V.G. micromass 12B spectrometer coupled to a Pye 104 gas chromatograph.

Elemental analyses were carried out with a Perkin-Elmer 240 CHN analyser.

Gas chromatography analysis was carried out using a Pye Unicam GCD gas chromatograph (flame ionisation detector).

Preparative scale gas chromatography was carried out using a Varian Aerograph Model 920 chromatograph.

N.m.r. spectra were recorded on either a:

- (i) Varian EM360L spectrometer (56.4MHz for  $^{19}\text{F}$ , 60.00 MHz for  $^1\text{H}$ ),
- (ii) Bruker WH-90 FT spectrometer (22.63MHz for  $^{13}\text{C}$ ), or
- (iii) *via* the SERC High Field N.m.r. services at Edinburgh or Newcastle. The majority of the  $^{13}\text{C}$  n.m.r. spectra of polymers were obtained from the Edinburgh service.

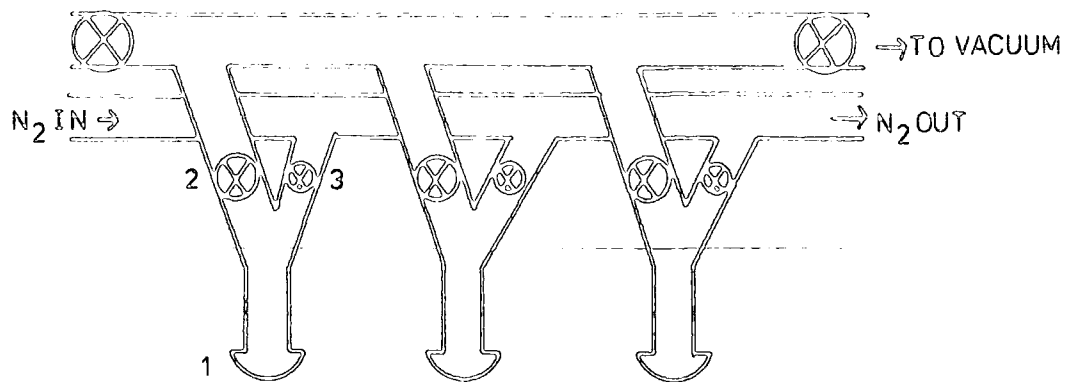
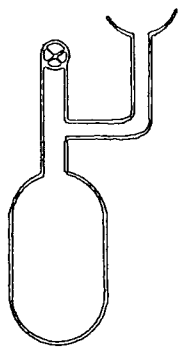
$^{19}\text{F}$  Chemical shifts are in ppm from external fluorotrichloromethane (positive upfield),  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are measured on the  $\delta$  scale relative to tetramethylsilane.

Differential scanning calorimetry was performed using a Perkin-Elmer DSC-2 Model B Differential scanning calorimeter.

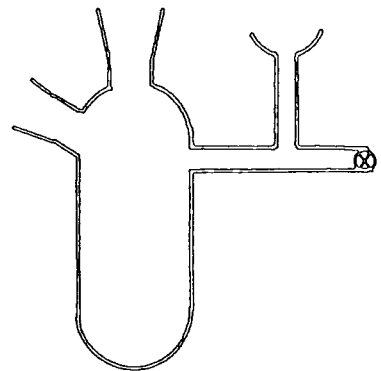
Thermogravimetric analysis was performed using a Stanton Redcroft TG760 thermobalance operating in percentage weight loss mode.

Gel permeation chromatography was carried out using PL gel columns of  $10^5$ ,  $10^3$  and  $500\text{\AA}$  pore size arranged in series. Each column was 300nm x 7.7mm diameter and 38,000 plates/m. Tetrahydrofuran, which had been distilled, degassed and stabilised was used as solvent.

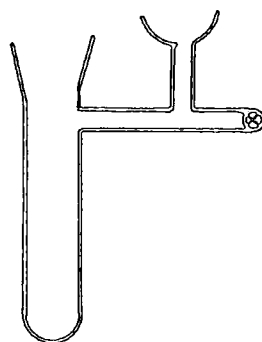
Vacuum System. A vacuum/dry nitrogen line, of the type depicted below was used. All joints are greasefree, fitted with Young's teflon taps and 'O' rings. An Edwards E2M-1.5 two stage high vacuum pump was used and pressures were measured using an Edwards PR10-C Pirani head and Pirani 11 gauge.

Vacuum/dry nitrogen lineApparatus

Flask 1



Flask 2



Flask 3

APPENDIX B  
INFRARED SPECTRA

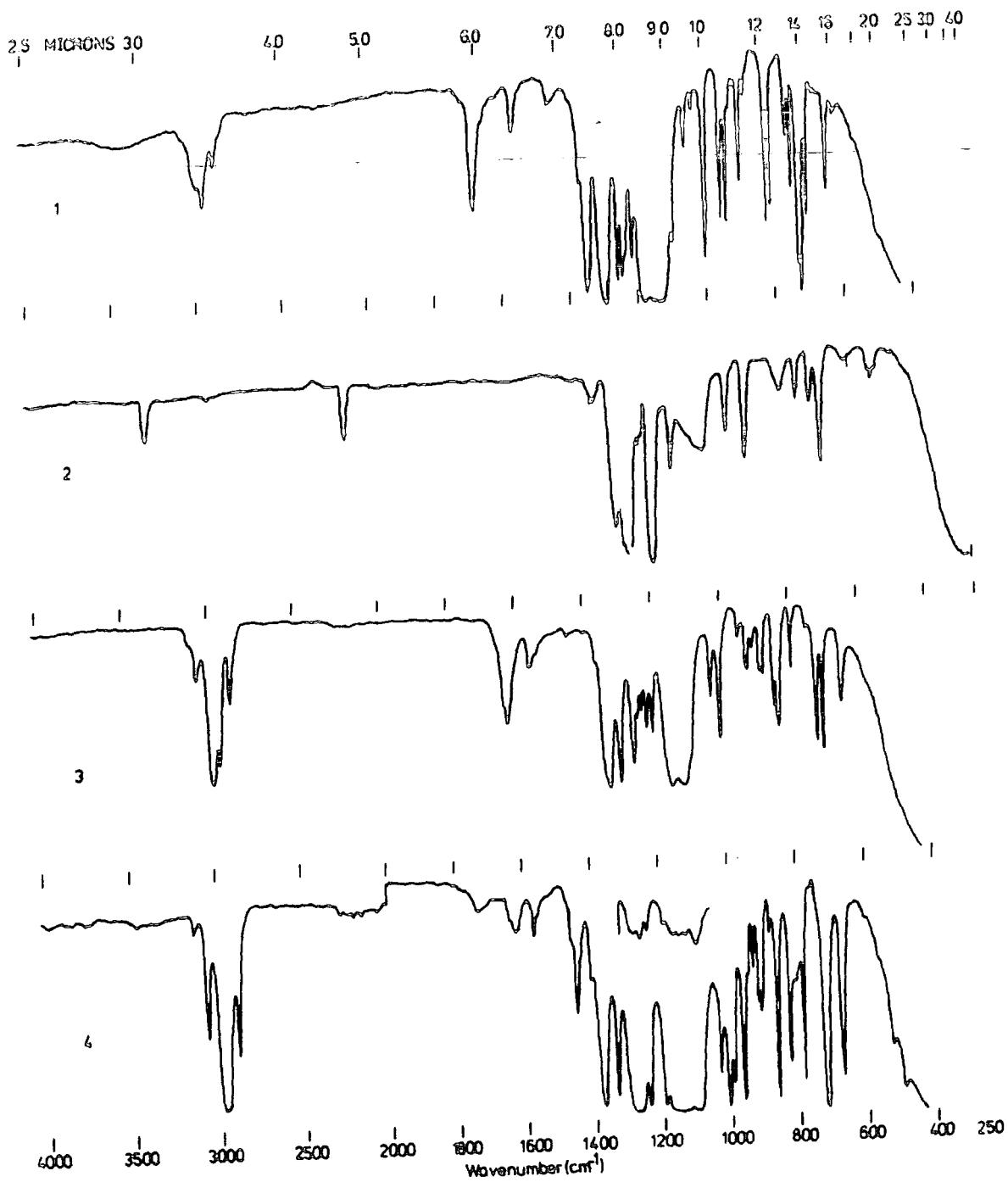
Infrared spectra are given below. All spectra were recorded using KBr cells, plates or discs, and were run under conditions designated by:

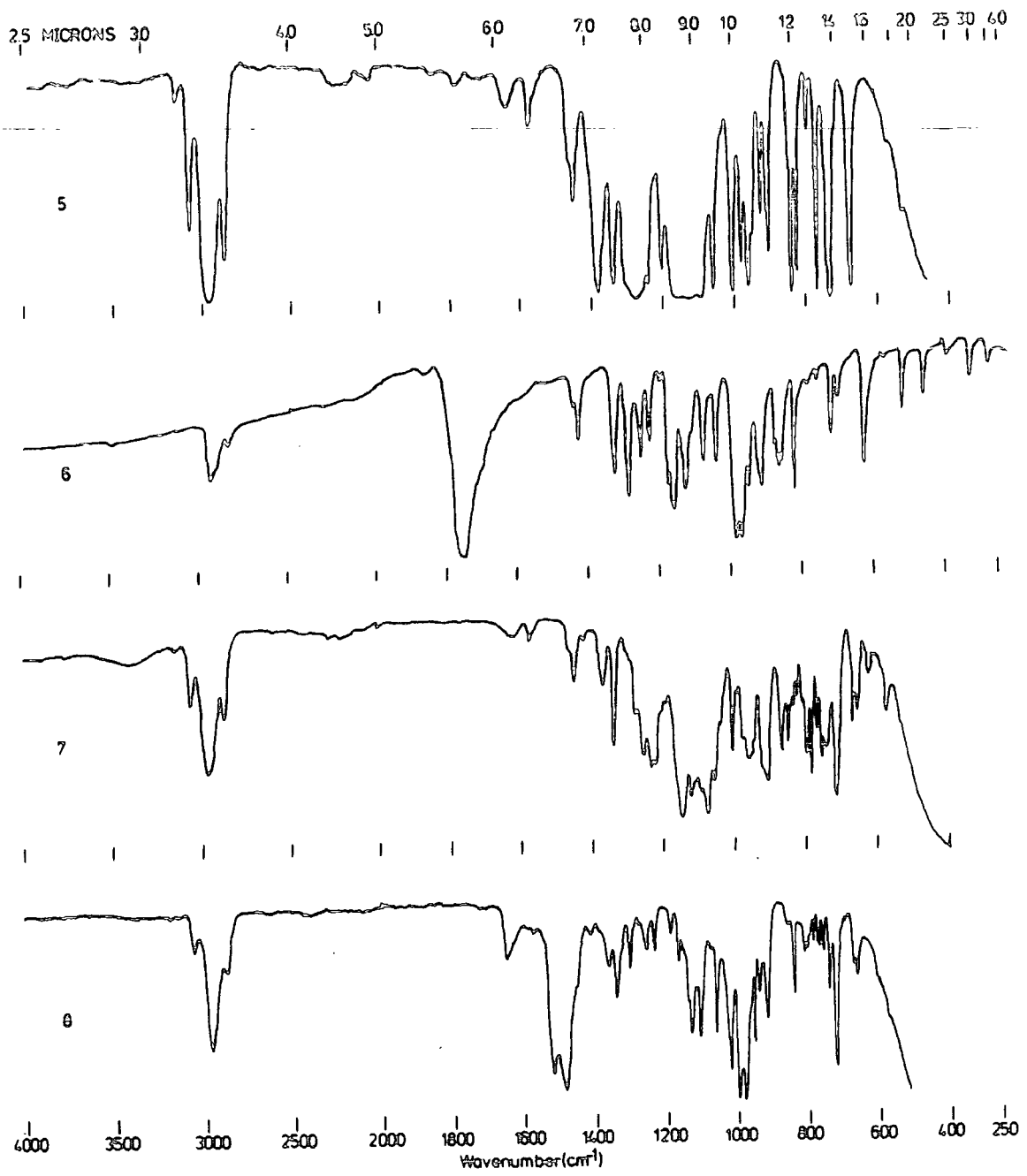
- (A) - KBr disc
- (B) - thin liquid film
- (C) - gas phase.

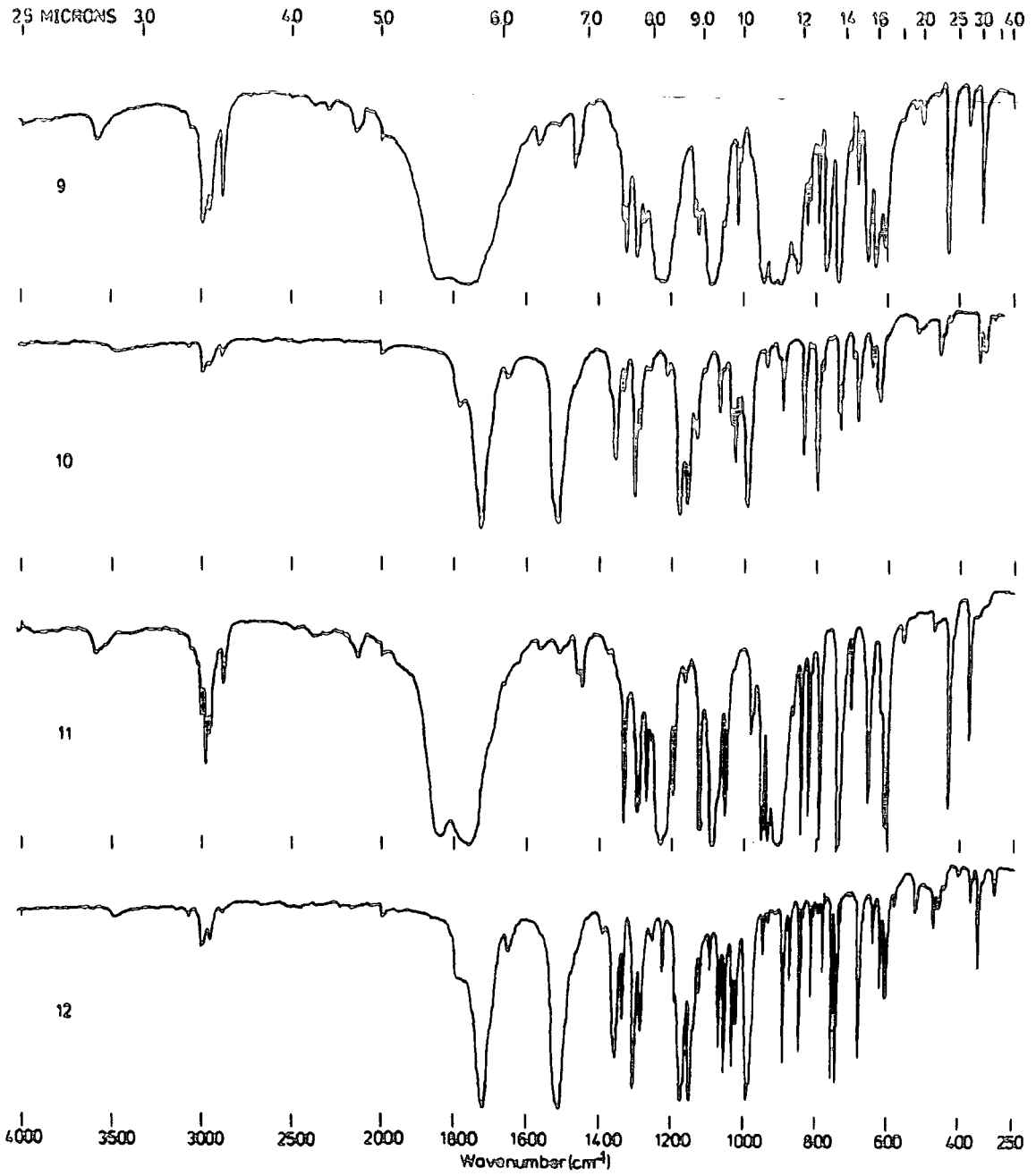
Spectrum No.Name of Compound

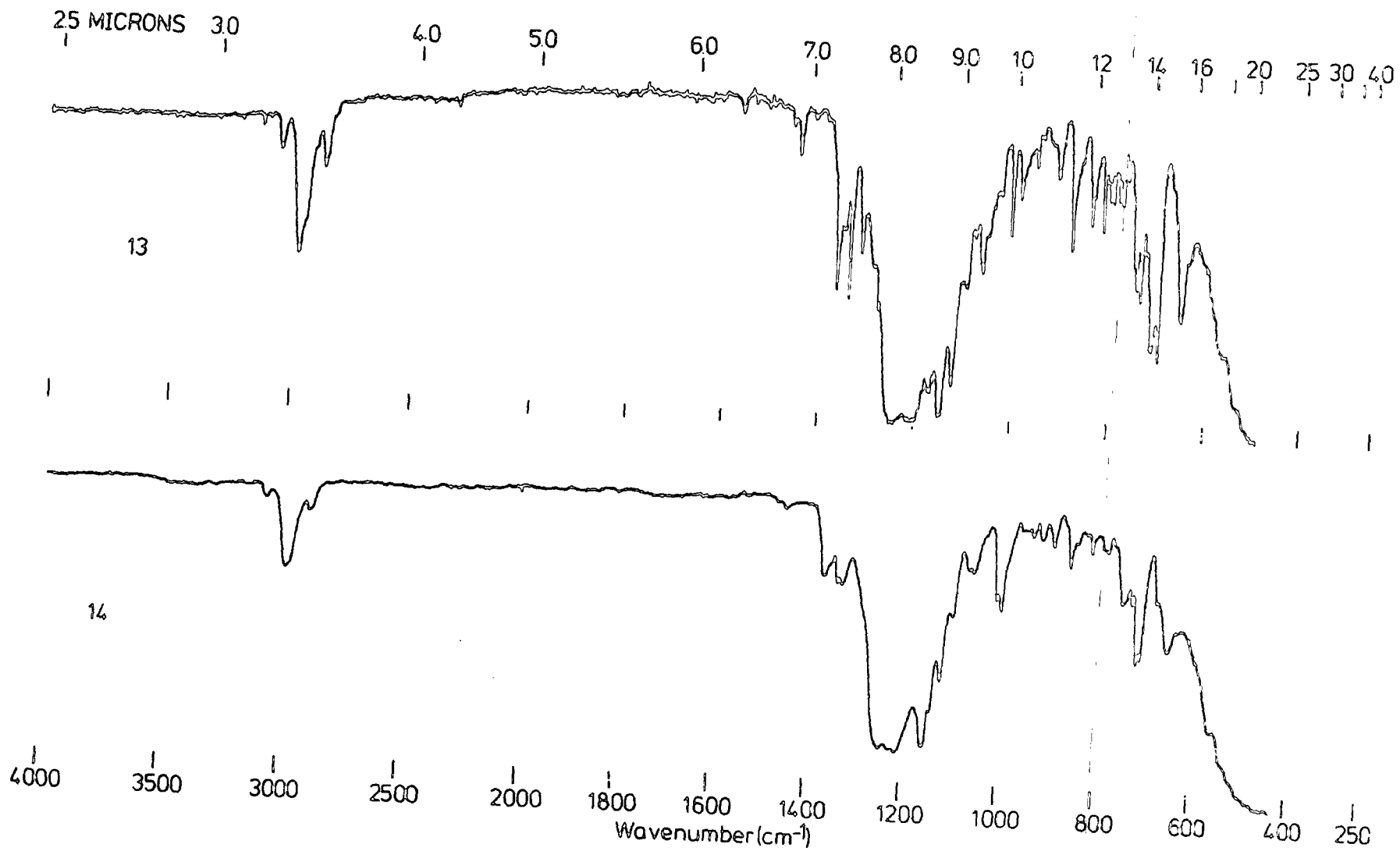
1. 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (B)
2. 3,3,3-trifluoropropyne (with PCT) (C)
3. 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene (B)
4. endo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene (B)
5. exo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene (B)
6. iodolactone of 5-carboxybicyclo[2.2.1]hept-2-ene (A)
7. 5-(2'-bromotetrafluoroethyl)bicyclo[2.2.1]hept-2-ene (B)
8. 5-pentafluorophenylbicyclo[2.2.1]hept-2-ene (B)
9. exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy-anhydride (A)
10. exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (A)
11. endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy-anhydride (A)
12. endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (A)
13. 5-perfluorohexylbicyclo[2.2.1]hept-2-ene (B)
14. 5-perfluorooctylbicyclo[2.2.1]hept-2-ene (B).











APPENDIX C

MASS SPECTRA

The mass spectra of compounds obtained in the course of this work are tabulated below. Ions are tabulated in the form:

134 (27%,  $C_6H_5F_3$ ,  $M-C_2H_2$ ).

In this example the ion has a mass number 75, its intensity is 27% of the intensity of the base peak, it has provisionally been assigned the formula  $C_6H_5F_3$ , and its origin is loss of  $C_2H_2$  from the parent ion  $M$ . The base peak is designated B.

1. 2-Trifluoromethylbicyclo[2.2.1]hepta-2,5-diene

160 (26%,  $C_8H_7F_3$ ,  $M$ ), 159 (20%,  $C_8H_6F_3$ ,  $M-H$ ), 140 (5%,  $C_8H_6F_2$ ,  $M-HF$ ), 134 (27%,  $C_6H_5F_3$ ,  $M-C_2H_2$ ), 114 (10%,  $C_8H_4F_2$ ,  $M-C_2H_2.HF$ ), 109 (11%,  $C_7H_6F$ ,  $M-CF_2H$ ), 91 (100%,  $C_7H_7$ ,  $B, M-CF_3$ ), 66 (15%,  $C_5H_6$ ), 65 (19%,  $C_5H_5$ ).

2. Endo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene

162 (2%,  $C_8H_9F_3$ ,  $M$ ), 93 (4%,  $C_7H_9$ ,  $M-CF_3$ ), 91 (5%,  $C_7H_7$ ,  $M-CH_2F_3$ ), 67 (6%,  $C_5H_7$ ), 66 (100%,  $C_5H_6$ ,  $B$ ), 65 (5%,  $C_5H_5$ ).

3. Exo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene

162 (2%,  $C_8H_9F_3$ ,  $M$ ), 93 (6%,  $C_7H_9$ ,  $M-CF_3$ ), 91 (5%,  $C_7H_7$ ,  $M-CH_2F_3$ ), 67 (7%,  $C_5H_7$ ), 66 (100%,  $C_5H_6$ ,  $B$ ), 65 (6%,  $C_5H_5$ ).

4. 5-(2'-Bromotetrafluoroethyl)bicyclo[2.2.1]hept-2-ene

274 (2%,  $C_9H_9F_4$   $^{81}Br$ ,  $M$ ), 272 (2%,  $C_9H_9F_4$   $^{79}Br$ ,  $M$ ), 193 (2%,  $C_9H_9F_4$ ,  $M-Br$ ), 174 (2%,  $C_9H_9F_3$ ,  $M-BrF$ ), 143 (6%,  $C_8H_9F_2$ ,  $M-CF_2Br$ ), 131 (1%,  $^{81}CF_2Br$ ), 129 (1%,  $^{79}CF_2Br$ ), 93 (30%,  $C_7H_9$ ,  $M-CF_2CF_2Br$ ), 91 (23%,  $C_7H_7$ ,  $M-C_2H_2F_4Br$ ), 78 (12%,  $C_6H_6$ ), 77 (55%,  $C_6H_5$ ), 67 (51%,  $C_5H_7$ ), 66 (100%,  $C_5H_6$ ,  $B$ ).

5. 5-Pentafluorophenylbicyclo[2.2.1]hept-2-ene

260 (1%,  $C_{13}H_9F_5$ , M), 259 (1%,  $C_{13}H_8F_5$ , M-H), 194 (18%,  $C_8H_3F_5$ , M- $C_5H_6$ ), 193 (14%,  $C_8H_2F_5$ , M- $C_6H_6$ ), 181 (11%,  $C_7H_2F_5$ , M- $C_6H_7$ ), 169 (2%,  $C_6H_2F_5$ , M- $C_7H_7$ ), 78 (11%,  $C_6H_6$ ), 66 (100%,  $C_5H_6$ , B), 65 (31%,  $C_5H_5$ , B-H).

6a. Endo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide

329 (1%,  $C_{15}H_8F_5NO_2$ , M), 328 (1%,  $C_{15}H_7F_5NO_2$ , M-H), 263 (12%,  $C_{10}H_2F_5NO_2$ , M- $C_5H_6$ ), 262 (6%,  $C_{10}H_1F_5NO_2$ , M- $C_5H_7$ ), 149 (1%,  $C_9H_8O_2$ , M- $C_6F_5N$ ), 92 (7%,  $C_7H_8$ ), 91 (23%,  $C_7H_7$ ), 67 (15%,  $C_5H_7$ ), 66 (100%,  $C_5H_6$ , B), 65 (19%,  $C_5H_5$ , B-H).

6b. Exo-N-pentafluorophenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide

329 (35%,  $C_{15}H_8F_5NO_2$ , M), 328 (10%,  $C_{15}H_7F_5NO_2$ , M-H), 263 (69%,  $C_{10}H_2F_5NO_2$ , M- $C_5H_6$ ), 262 (18%,  $C_{10}H_1F_5NO_2$ , M- $C_5H_7$ ), 181 (2%,  $C_6F_5N$ , M- $C_9H_8O_2$ ), 92 (21%,  $C_7H_8$ ), 91 (68%,  $C_7H_7$ ), 67 (30%,  $C_5H_7$ ), 66 (100%,  $C_5H_6$ , B), 65 (41%,  $C_5H_5$ , B-H).

7. 5-Perfluorohexylbicyclo[2.2.1]hept-2-ene

412 (1%,  $C_{13}H_9F_{13}$ , M), 392 (1%,  $C_{13}H_8F_{12}$ , M-HF), 93 (15%,  $C_7H_9$ , M- $(CF_2)_5CF_3$ ), 77 (11%,  $C_6H_5$ ), 67 (10%,  $C_5H_7$ ), 66 (100%,  $C_5H_6$ , B).

8. 5-Perfluorooctylbicyclo[2.2.1]hept-2-ene

492 (1%,  $C_{15}H_8F_{16}$ , M-HF), 143 (1%,  $C_8H_9F_2$ , M- $(CF_2)_6CF_3$ ), 93 (6%,  $C_7H_9$ , M- $(CF_2)_7CF_3$ ), 77 (6%,  $C_6H_5$ ), 67 (6%,  $C_5H_7$ ), 66 (100%,  $C_5H_6$ , B).

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