THE SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NEW ORGANOMETALLIC POLYMERS

A thesis submitted to the

UNIVERSITY OF CAPE TOWN

in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

by

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February 1996

ACKNOWLEDGEMENTS

My sincere thanks and appreciation are extended to:

My supervisor, Professor J. R. Moss, for introducing me to organometallic chemistry, and for his firm support and guidance during the course of this project.

My colleagues and friends in the Department of Chemistry, especially Dr J. M. Andersen, Dr Y. H. Liao, Miss M. Timme, Miss R. George, Miss F. Waggie, Miss S. J. Hughes, Mr O. Hill, Mr E. Starr, Mr J. Mare, Mr H. Clayton, Mr X. Yin, Mr P. Galatolo for their support and friendship.

Miss M. Nair and Mr N. Hendricks for recording NMR spectra, Miss R. Mohammed for recording the DSC and TGA, Mr M. A. Jaffer for running the TEM, Mr M. A. Gafoor and Miss M. P. van Alphen [Vynide (Pty) Ltd] for use of their SEC instruments.

The University of Cape Town and FRD for financial support.

My wife, Debbie for all her love, understanding, and support.

My daughter, Eileen for being as sweet as ever.

ABSTRACT

We have reviewed recent work on highly branched polymers called dendrimers.

Two novel block copolymers consisting of organoruthenium dendritic wedges and linear polyethylene glycol blocks have been prepared. These new block copolymers have been characterized by IR, ^1H and ^{13}C NMR, microanalysis, as well as size exclusion chromatography. The SEC results of some very large organoruthenium dendrimers are also discussed. The thermal properties of these block copolymers have been studied by differential scanning calorimetry and thermogravimetric analysis. The morphology of these block copolymers have been studied by transmission electron microscopy. We also describe a preliminary thin film study,resulting from the decomposition of some of the block copolymers.

Two ruthenium and platinum complexes containing bulky dendritic phosphine ligands, cis-$Pt(RDP)_2Cl_2$ and trans,trans,trans-$RuCl_2(CO)_2(RDP)_2$, have been prepared. These new phosphine complexes have been characterized by IR, ^1H, ^{13}C and ^{31}P NMR, as well as elemental analysis. We also discuss the potential catalytic application of these dendritic phosphine metal complexes in the hydroformylation reaction.

CONFERENCE CONTRIBUTIONS

1. Poster titled "The synthesis, characterization, and properties of ruthenium-containing organometallic dendrimers and potential applications in catalysis", R. Zeng, Y.H. Liao, and J. R. Moss, presented at the Annual Conference of the South African Catalysis Society in Pretoria, RSA (1994).

2. Poster titled "The synthesis and characterization of novel organometallic polymers", R. Zeng and J. R. Moss, presented at "Inorganic'95" in Pietermaritzburg, RSA (1995).

3. Poster titled " The synthesis and characterization of new organoruthenium dendrimers: towards the development of heterogenized homogeneous catalysts", R. Zeng and J. R. Moss, presented at "Catalysis and Catalytic Processing" in Rustenburg, RSA (1995).

ABBREVIATIONS

COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
DSC	differential scanning calorimetry
EI	electron impact
FAB	fast atom bombardment
IR	infrared spectroscopy
Me	methyl group
L	ligand(s)
m.p.	melting point
NMR	nuclear magnetic resonance spectroscopy
Ph	phenyl
RDP	ruthenium-containing dendritic phosphine
SEC	size exclusion chromatography
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMS	tetramethysilane

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CHAPTER 3 THE SYNTHESIS, CHARACTERIZATION, AND POTENTIAL APPLICATION OF NOVEL RUTHENIUM-CONTAINING DENDRITIC PHOSPHINE METAL COMPLEXES

Chapter 1 A review of recent work on highly branched polymers called dendrimers

1.1 Introduction and background

" Chemistry is not just a science involving the study of electron movement to rearrange and connect atoms. It is a philosophy, a way of thinking about the world, about how matter is constructed, organized, and how it functions throughout the dimensional hierarchy of the universe, from the simplest atoms to the most complex pheonomena - namely life itself. "[1] Particularly in polymer science, polymer scientists are turning their attention to more elaborate topologies. Highly branched polymers called dendrimers, which have accurately controlled macromolecular architectures, are one novel type that has attracted ever increasing attention in organic, supramolecular, and polymer chemistry, and also in recent years in coordination chemistry .[2-10] Several extensive review articles on dendrimers have appeared recently.[11-20]

The word dendrimer is derived from the Greek word "dendron " meaning " tree " and the last syllable in the word polymer.[12] Dendrimers are also known variously as cascades,[21] starbursts,[22] or arborol polymers.[23] Structurally, dendrimers are characterized by several chains growing from a polyfunctional core molecule. As the chains extend outward, they branch regularly and frequently, resulting in a three dimensional and entanglement free spherical or globular architecture. As the molecular weight of dendrimers increases, they adopt an increasingly globular shape, the surface of which is made up of a large number of chain ends or functional groups.

Ideally all the chains grow equally and the final structure is a close-packed molecular ball with many surface end groups. See Figure 1.1 below.

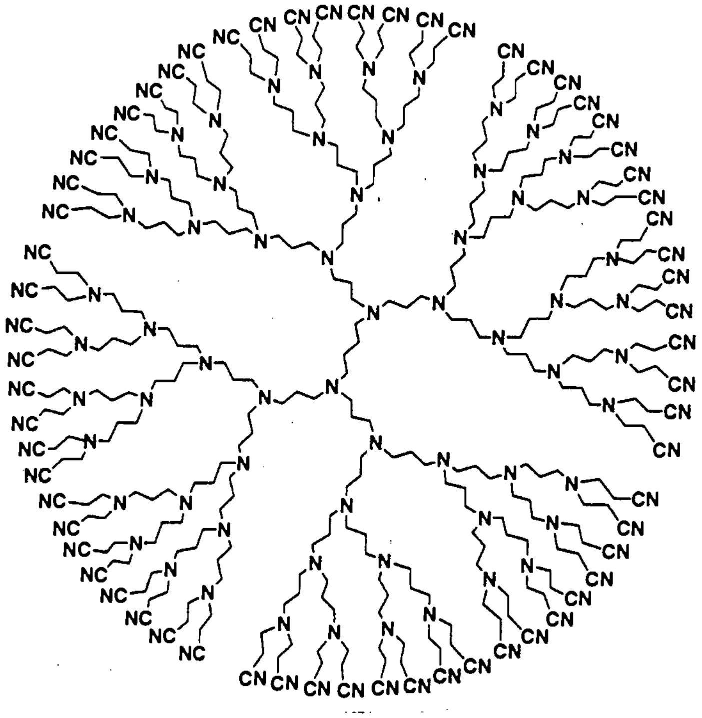


Figure 1.1 Representation of a dendrimer

The increasing interest in dendrimers is due to their novel highly branched, three dimensional globular architecture which is so different from that of traditional linear step -growth polymers. In contrast to linear polymers, which are one long chain with only two end groups, dendrimers have many short chains, a very high degree of branching and large number of chain ends (normally hundreds) exclusively at the periphery. Therefore, one would expect that the end groups would play an important role in the properties of these dendrimers, such as solubilities in organic solvents[24] or the glass transition temperature[25]. The interest in dendrimers is also due to their much higher degree of structural and molecular weight control. Because of their shape, dendrimers offer unusual new physical and chemical properties as well as new phenomena. For example, the intrinsic viscosity of dendrimers, in contrast to almost all other polymers, does not comply with the Mark-Houwink-Sakurada equation: $[\eta] = K M^{\alpha}$, in which $[\eta]$ is the intrinsic viscosity of the polymer, M is its molecular weight, and K and α are constants for a given polymer. As the molecular weight of dendrimers increases, the molecules undergo a transition from an extended to a dense spherical shape. This transition is readily observed in a plot of intrinsic viscosity versus molecular weight (or generation number),[26] see Figure 1.2 below.

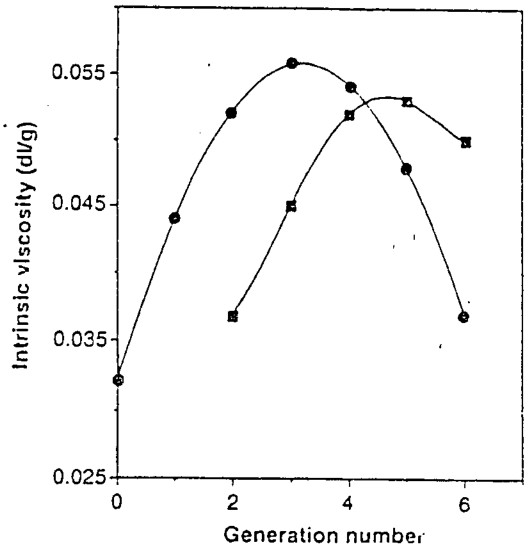


Figure 1.2 Plot of intrinsic viscosity versus generation number for typical polyether dendrimers[26]

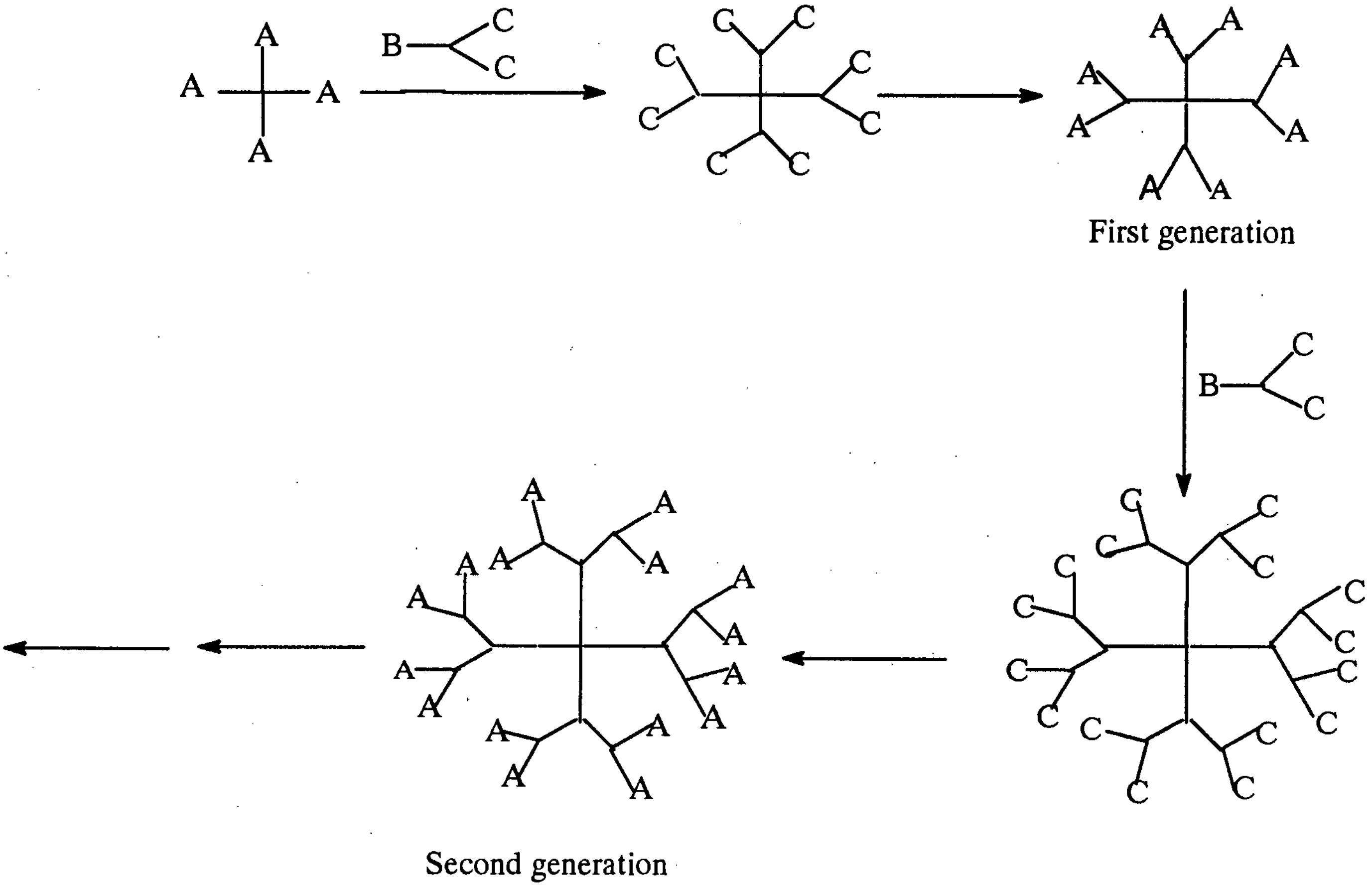
What potential new applications exist for this novel class of polymers ? One possibility is a delivery system for drug or agrochemicals; for example, polyamidoamine (PAMAM) dendrimers are already used as carriers for DNAs and carriers for peptide antigens.[27,28] Also, PAMAM can be used as carriers for agrochemicals, such as pesticides, radionuclide chelators, chelated metals, toxins, etc, by conjugating with them. This allows for high concentrations of the carried agrochemicals per unit dendrimer, for controlled and targeted delivery, and multiple-species delivery.[29] Another possibility is use as a catalyst carrier system. At Utrecht University and Shell Research BV in the Netherlands, van Koten and coworkers have synthesized the first dendrimer-supported catalysts[30]. These catalysts are silane dendrimers functionalized with catalytically active arylnickel(II) complexes on the periphery. This new class of catalyst shows regiospecific catalytic activity for addition reactions of polyhalogenalkanes to carbon-carbon double bonds and combines the advantages of homogeneous and heterogeneous catalysts. In addition, these dendrimers also have a broad spectrum of potential applications for example in host-guest chemistry,[9] ion exchange materials,[31] recyclable solubilization agents,[32] molecular antenna,[35] magnetic resonance imaging contrast agents,[34] liquid-crystals,[35,36] engineering plastics,[37] and many more.

1.2 Synthetic methodology for dendrimers

To construct a perfect highly branched dendrimer requires a very carefully controlled synthetic methodology. Normally dendrimers are constructed by a controlled stepwise manner, in which chain propagation is by repeated coupling and activation reactions. Each reaction cycle creates a new "generation" . Two fundamentally different synthetic approaches have been developed to synthesize dendrimers: one is a divergent approach in which the direction of chain growth is from the center outwards, the other is a convergent approach in which the direction of chain growth is from the periphery inwards.

Divergent methodology This synthetic methodology was independently developed by

Tomalia[38] and Newkome,[39] best known for the preparation of "starburst" and "arborol" dendrimers in the mid 1980's. The divergent growth strategy involves the initial reaction of a polyfunctional core molecule with an BCx monomer unit which contains at least two protected branching sites. After purification, the second step involves deprotection of the branching sites which regenerates the reaction chain ends or branching sites to give the next generation dendritic macromolecule. Repetition of this two step process allows growth to proceed radially outward with a rapid increase in the number of reactive groups at the chain ends of the growing macromolecules. This is shown in Scheme 1.1



Scheme 1.1 Building up a dendrimer by divergent methodology

Advantages of the divergent methodology are the rapid growth of the dendrimer series and an increase in mass of isolated products with significant steric inhibition at early generations. Using this synthetic approach it is possible to construct up to tenth generation dendrimers with molecular weights of up to 700,000 amu and with more than 3,000 end groups per macromolecule.[5] It is also possible to synthesize these dendrimers in large quantities, even in multikilogram lots.[7] Several novel applications of this divergent methodology have recently appeared. Some of successful examples are given below.

Tomalia and co - workers have prepared a series of highly branched polyamidoamine dendrimers by this approach up to the tenth generation with a nominal molecular weight of 700,091.[13] The structure of a third generation polyamidoamine dendrimer is shown in Figure 1.3.

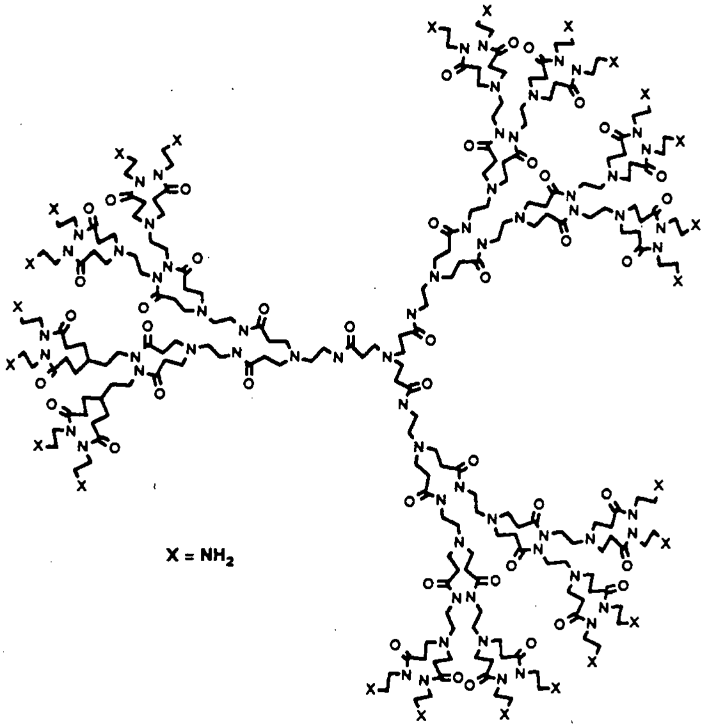
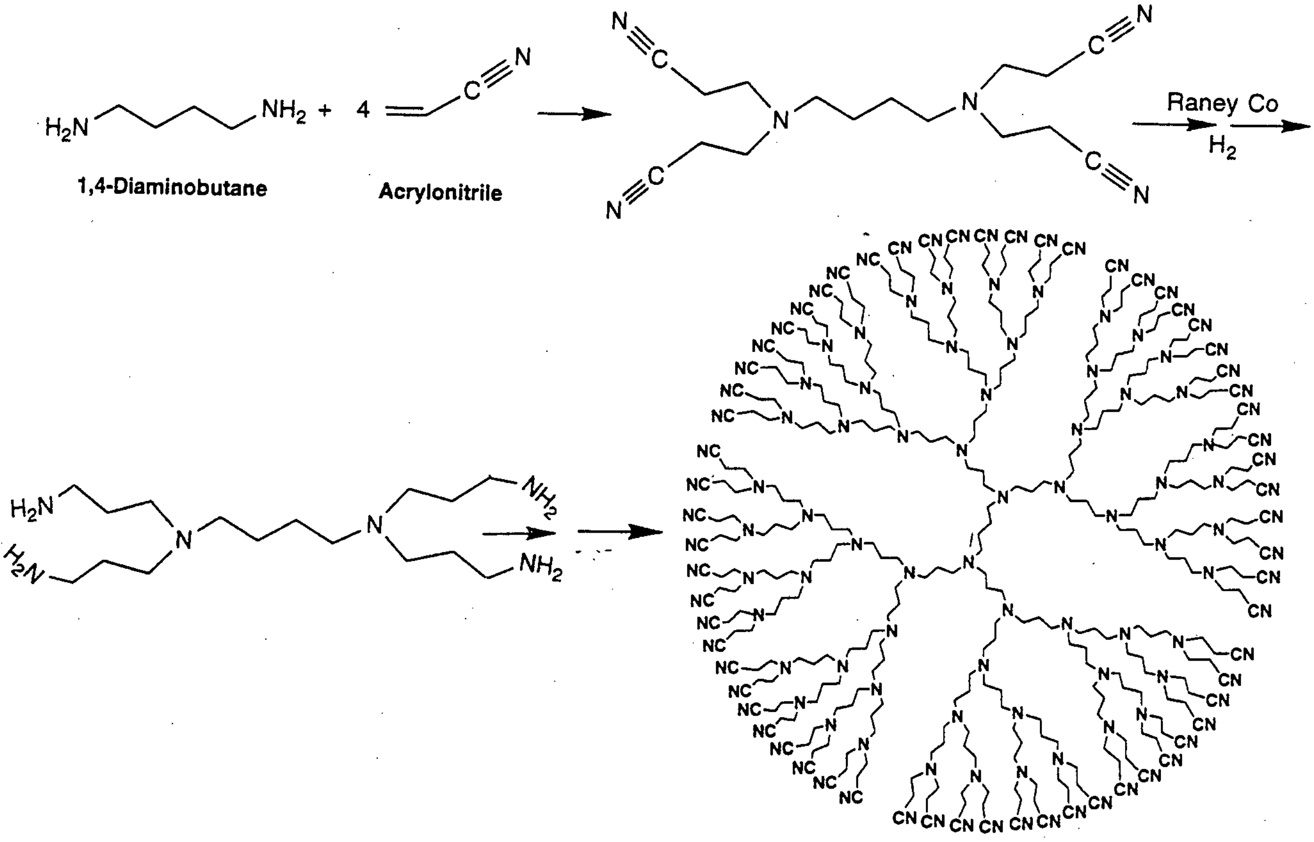


Figure 1.3 A third generation polyamidoamine dendrimer (PAMAM)

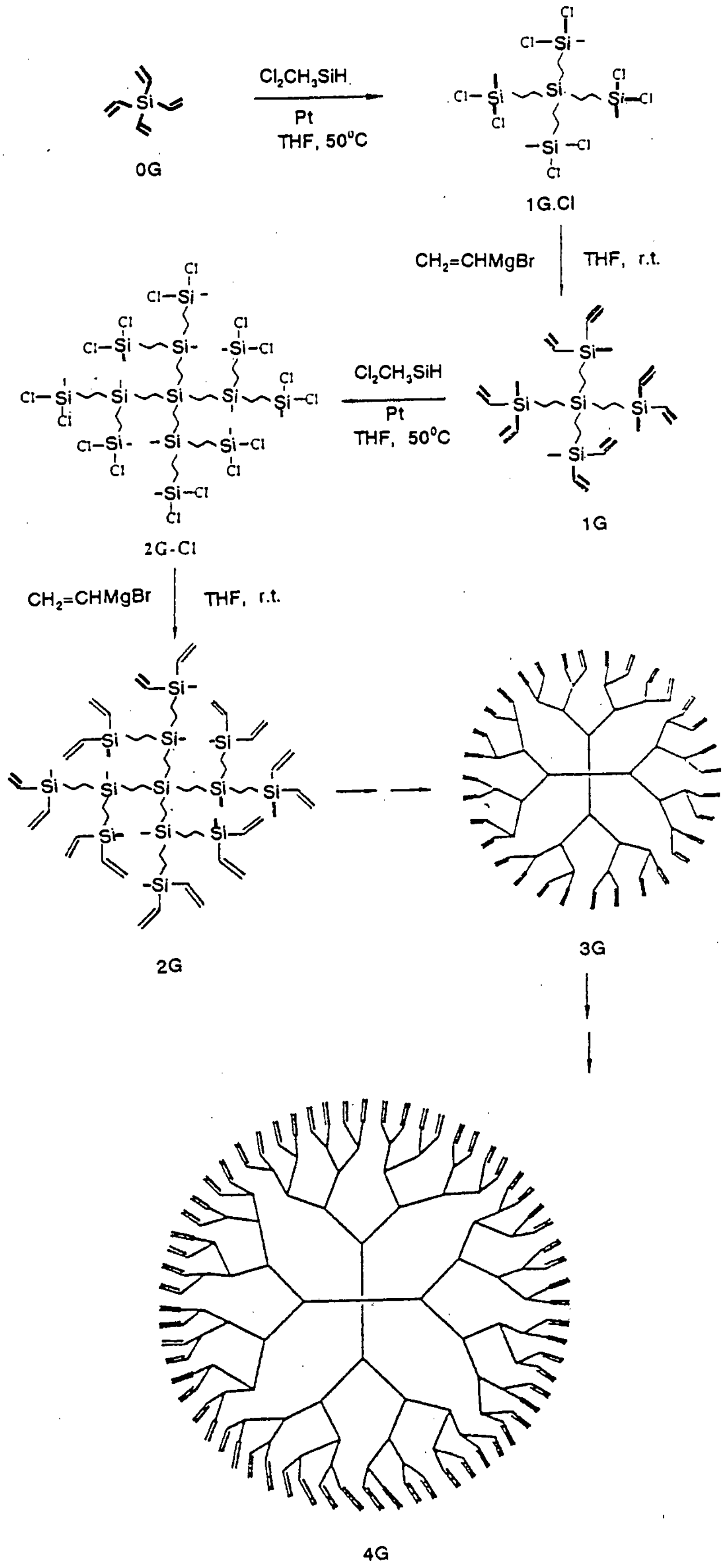
In the Netherlands, DSM researchers have synthesized multikilogram quantities of a poly(propylenimine) series of dendrimers by the divergent approach.[40] The reaction sequence shown in Scheme 1.2 is based on repetitive reaction of a primary amine with acrylonitrile, using the Michael addition reaction, followed by a heterogeneously catalyzed hydrogenation using hydrogen and Raney cobalt.



Scheme 1.2 Synthetic scheme for poly(propylene imine) dendrimers with 1,4-diaminobutane as core[40]

Recently, Zhou and Roovers have reported that up to the fourth generation carbosilane dendrimers have been synthesized by the divergent approach.[41] In the synthesis, tetravinylsilane is used as the initial core molecule. Two important reactions are involved in the synthesis of each generation: hydrosilylation of vinylsilane with dichloromethylsilane as propagation unit and nucleophilic replacement of silicon chloride by vinylmagnesium bromide. See Scheme 1.3 below.

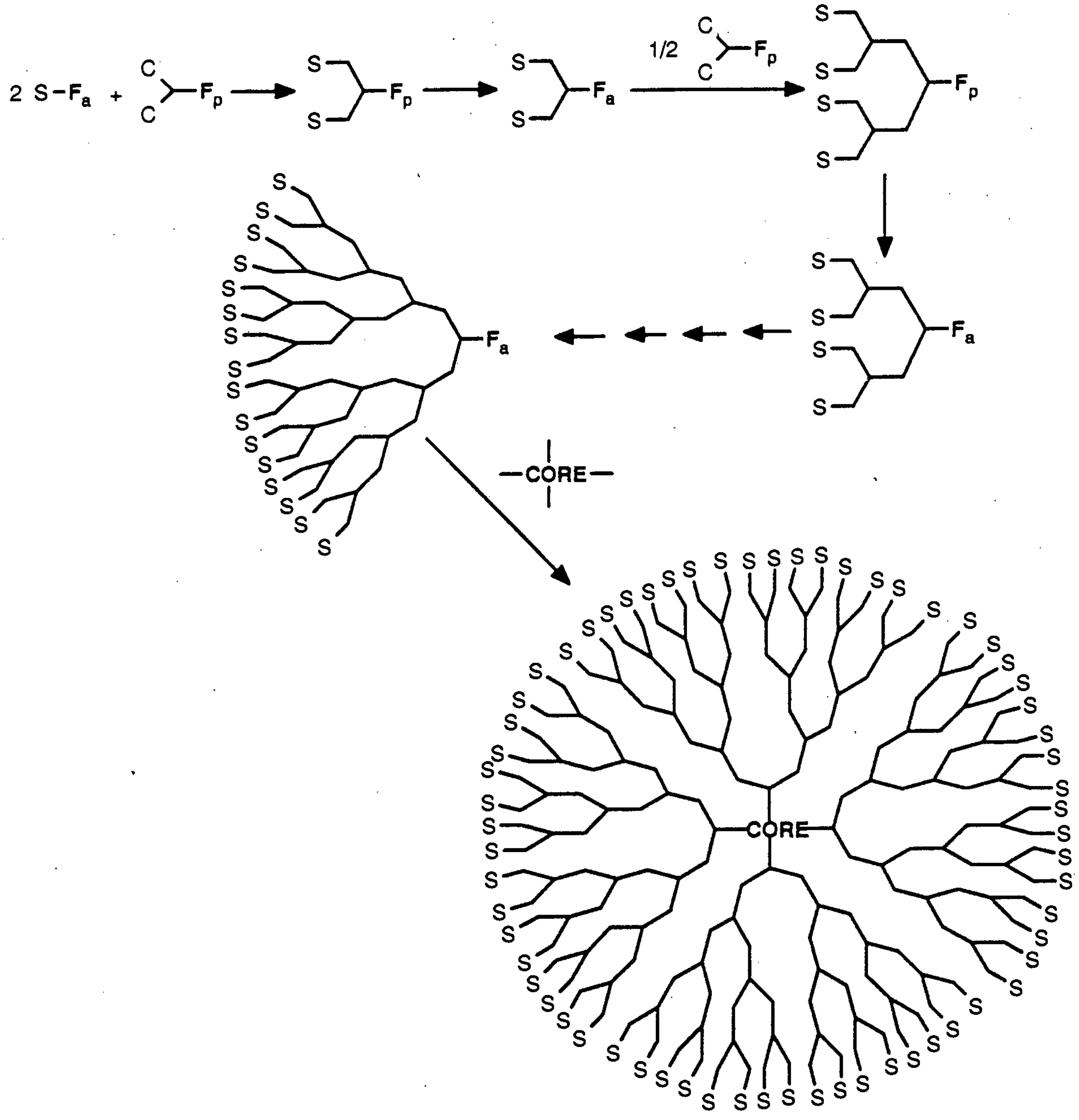
However, this divergent methodology has its limiting features: firstly, any incomplete reaction of these terminal groups would lead to imperfections in the next generation - the probability of this occurring increases as the growing macromolecule increases. Secondly, to prevent side reactions such as the coupling of " starburst " molecules and to force reactions to completion, extremely large excess amounts of reagents are required in latter stages of growth. This in turn leads to added difficulties maintaining monodispersity and purification.



Scheme 1.3 Synthetic scheme for the fourth generation carbosilane dendrimers[41]

Convergent methodology The convergent methodology was principally developed by Hawker and Fréchet[42-45] and Miller and Neenan[46,47] in 1990. This new synthetic approach not only overcomes the difficulties associated with the divergent approach, but can provide extremely accurate control of molecular architecture. In this methodology, construction of the molecule is started at what will ultimately become a peripheral functional group, and in each step, growth is designed to occur inward via reaction of only a very limited number of reaction sites. Successive reaction cycles generate a dendritic wedge with a functional reaction group at the apex. The final step is to attach several of these wedges to a polyfunctional core molecule. The basic idea of this approach is shown in Scheme 1.4.

This convergent approach has several advantages such as control over peripheral functionality, involvement of a very limited number of reactive sites (typically three) for generation growth, avoidance of large excesses of reagents, essentially monodisperse products, ease of purification and ease of characterization by spectroscopic methods. All of these features help to greatly minimize the occurrence of ' defects ' in the final architecture. This approach also provides the ability to dramatically change molecular structure by using different polyfunctional cores for a given dendritic wedge. Perhaps, the greatest advantage of this methodology is that block copolymers such as either segment-block or layer-block dendritic copolymers and novel copolymers consisting of linear and dendritic blocks can be easily prepared.



Scheme 1.4 Building up a dendrimer by convergent methodology

Recently, several research groups have successfully applied the convergent methodology to synthesize organic and inorganic dendrimers. Fréchet and co-workers have synthesized various copolymers including a segment block copolymer, layer block copolymer and linear-dendritic block copolymer (see Figures 1.4-1.6). [44,48-50]

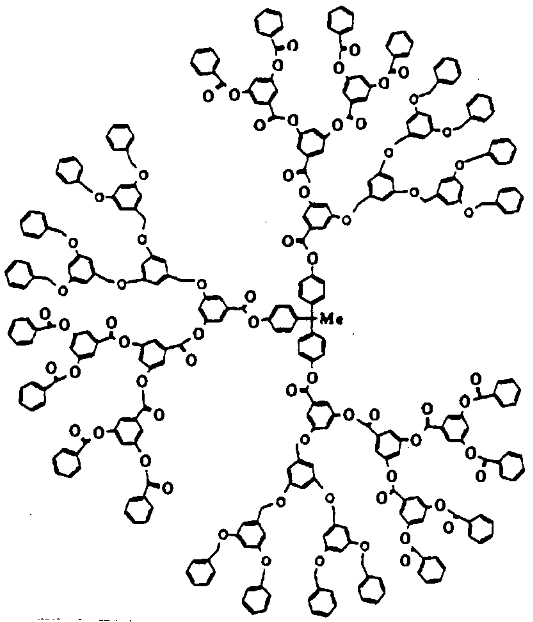


Figure 1.4 A segment block copolymer[48]

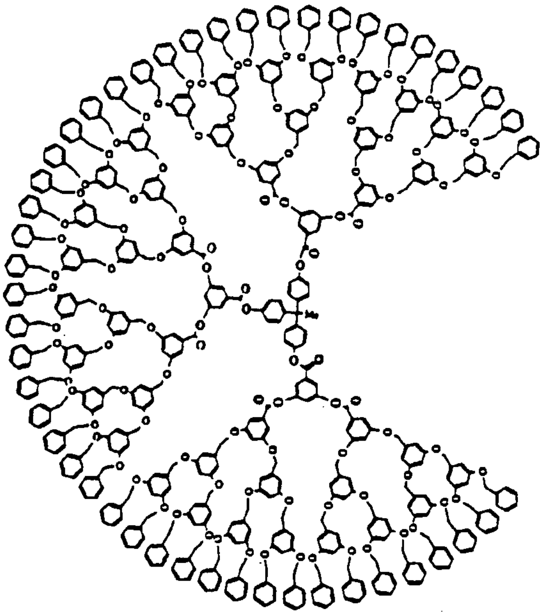


Figure 1.5 A layer block copolymer[48]

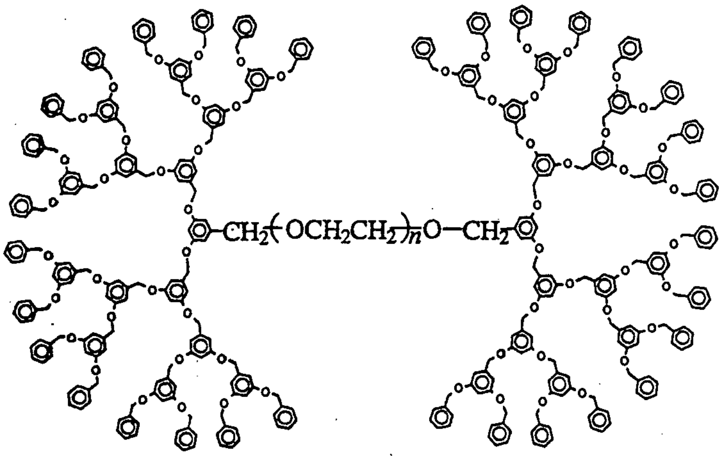


Figure 1.6 A linear-dendritic block copolymer[50]

Liao and Moss have recently synthesized the largest organotransition metal dendrimer containing 48 ruthenium atoms by convergent methodology.[51] It was constructed by reaction of three fourth generation dendritic wedges with a trifunctional core molecule, 1,1,1,-tris(4-hydroxyphenyl)ethane, and has a nominal molecular mass of 18,438 amu. A fourth generation organoruthenium dendritic wedge is shown in Figure 1.7.

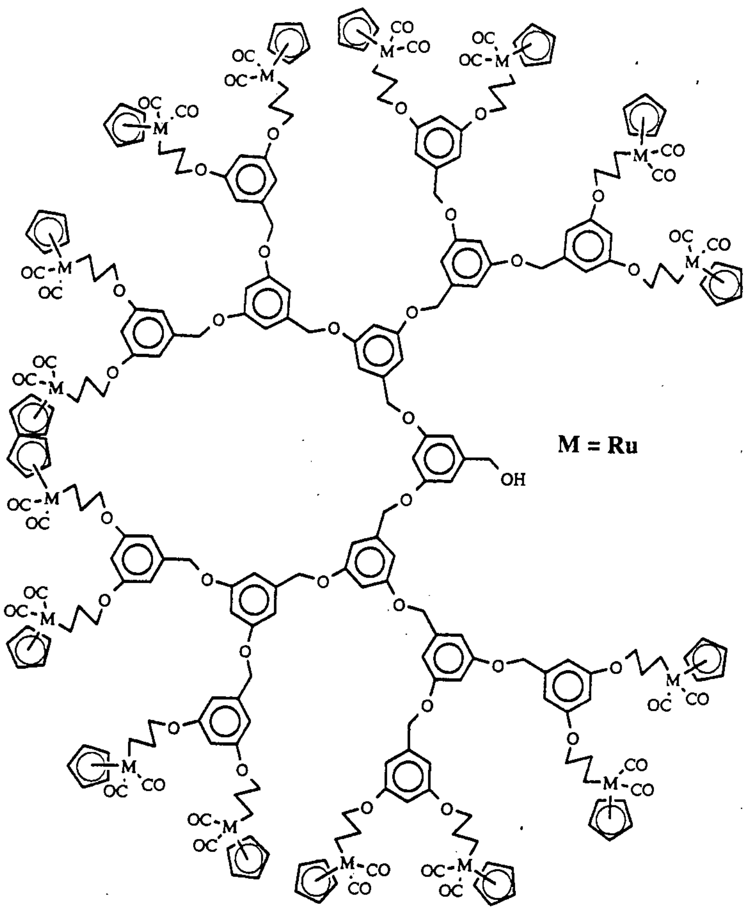


Figure 1.7 A fourth generation organoruthenium dendritic wedge[51]

One limitation of the convergent methodology is that, as the sizes of the dendrimers increase, they are increasing more susceptible to steric inhibition at the focal point, which tends to get internally buried. This effectively limits the size of the macromolecules that may be prepared in a conventional fashion.

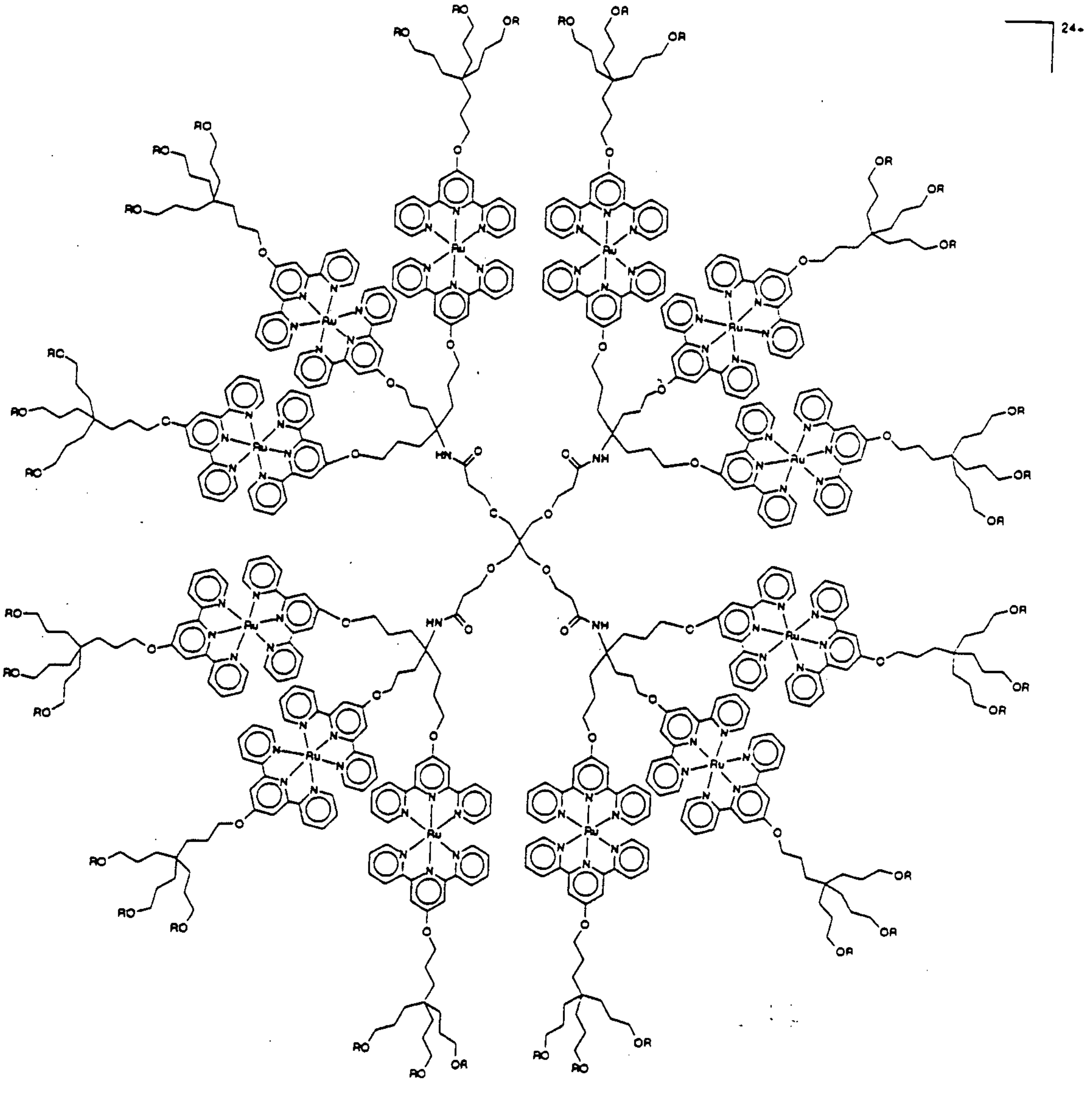
1.3 Inorganic dendrimers

Although the study of dendrimers has increased significantly since 1990, the majority of known dendrimers are organic in nature. Nevertheless, inorganic dendrimers which contain main group elements, or transition metals are also known.[52-56] Herein, we would like to summarize the inorganic dendrimers that have been prepared recently.

In 1993, Newkome and co - workers reported a series of dendrimers containing ruthenium terpyridine groups[57] and also a carborane[58] in a dendritic micellane (a unimolecular micelle) framework. Firstly, the dendritic structure was constructed by the divergent approach. The metal groups were then coordinated to the dendrimer, and the micellar property of the dendrimer was achieved in the subsequent reactions. The structure of ruthenium-containing dendrimer is shown in Figure 1.8.

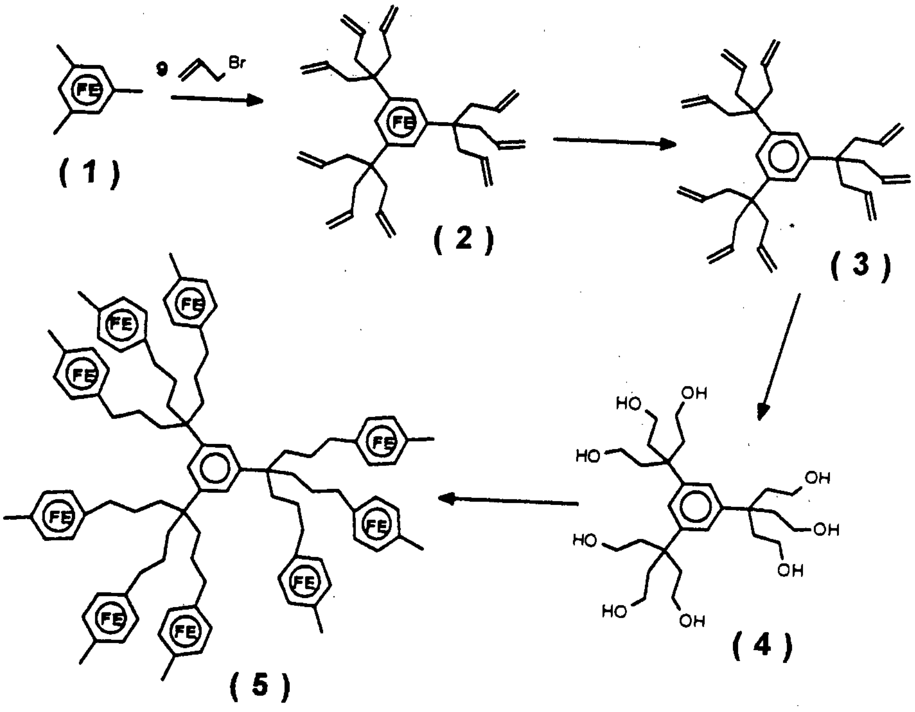
Also in 1993, Astruc and co - workers reported organometallic dendrimers containing $[CpFe(C_6R_6)]^+$ as multielectron and multiproton reservoirs.[59] These dendrimers were prepared by the divergent strategy, as shown in Scheme 1.5. The cyclic voltammograms of compound (5) show a reversible reduction wave for Fe^{II} (18 e) $\rightleftharpoons$ Fe^{I} (19 e). Thus, compound (5) is a reservoir of nine electrons and 27 benzylic protons.

In 1994, Fréchet and co - workers reported the preparation of a dendritic fullerene, by the controlled one-step cycloaddition reaction of a dendritic azide with C_{60}.[60] The structure of the dendrimer-modified C_{60} is shown in Figure 1.9. This dendritic fullerene proved to be extremely soluble in a variety of organic solvents, unlike C_{60}, and its glass transition temperature was found to be 13^{0}K higher than that of the starting dendrimer. This indicates that the physical properties of the dendritic fullerene show dramatic differences when compared to both the parent dendrimer and the fullerene portions.



R = $CH_2C_6H_5$

Figure1.8 A dendrimer containing ruthenium terpyridine groups[57]



FE = $(\mathrm{CpFe^{II}})^+ \ \mathrm{PF_6}^-$

Scheme 1.5 Synthetic scheme for dendrimers containing $[\mathrm{CpFe(C_6R_6)}]^+$groups[59]

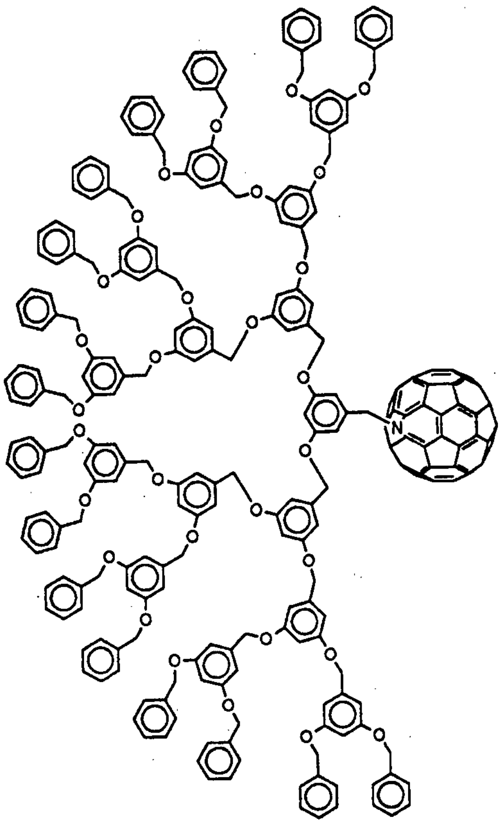


Figure 1.9 A dendritic fullerene[60]

In 1994, Shinkai and co - workers reported the first dendritic crown ether macromolecules successfully synthesized by the convergent approach.[61] The structure of a third generation dendrimer, containing 21 diaza-18-crown-6 units , is shown in Figure 1.10. Metal-binding studies show that the crown ether units behave independently. Shinkai also found that some of these dendrimers can solubilize proteins in organic solvents.

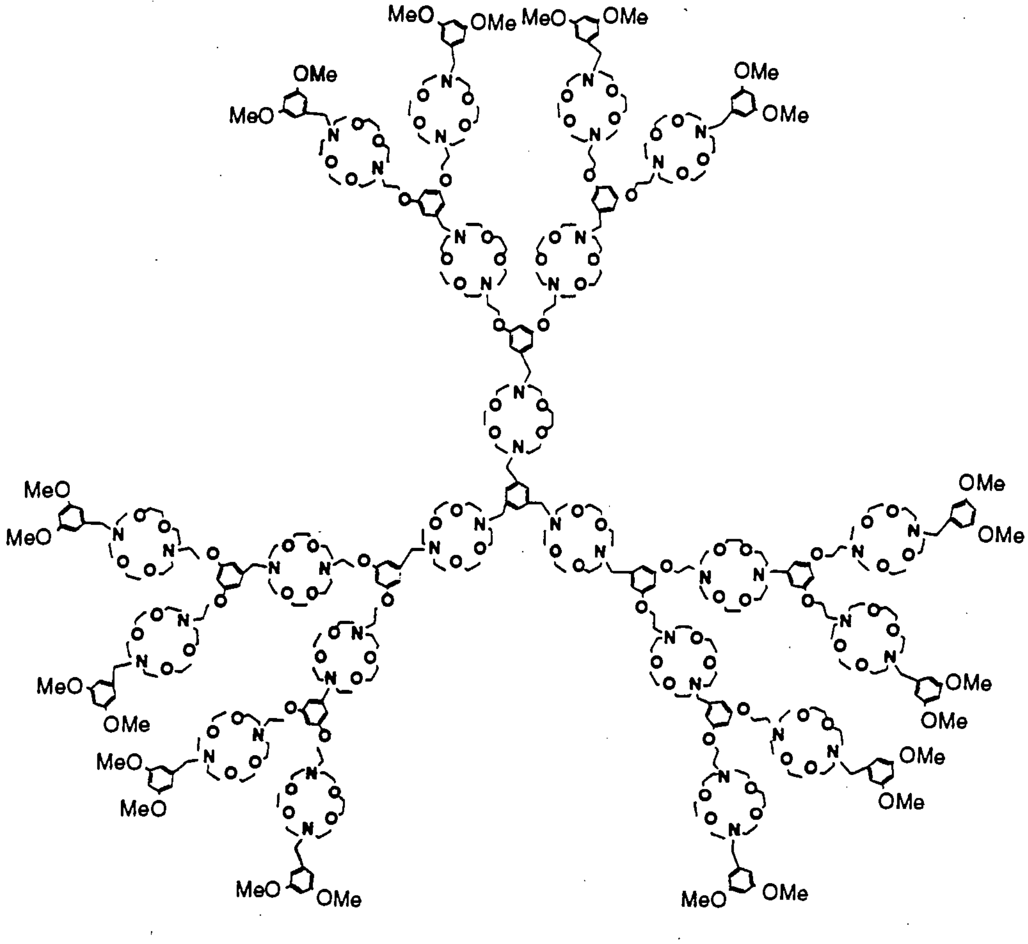


Figure 1.10 A dendritic crown ether[61]

In 1994, Majoral and co - workers reported the easy, high-yield preparation of neutral dendrimers up to the fourth generation in which the core and subsequent branch points are pentavalent phosphorous atoms.[62] The structure of such a fourth generation dendrimer is shown in Figure 1.11. These dendrimers possess, at the periphery, up to 48 of two of the most reactive functional groups in organic and main group element chemistry, namely aldehyde groups and phosphorus-chlorine bonds. These dendrimers may thus have applications in catalysis and coordination chemistry.

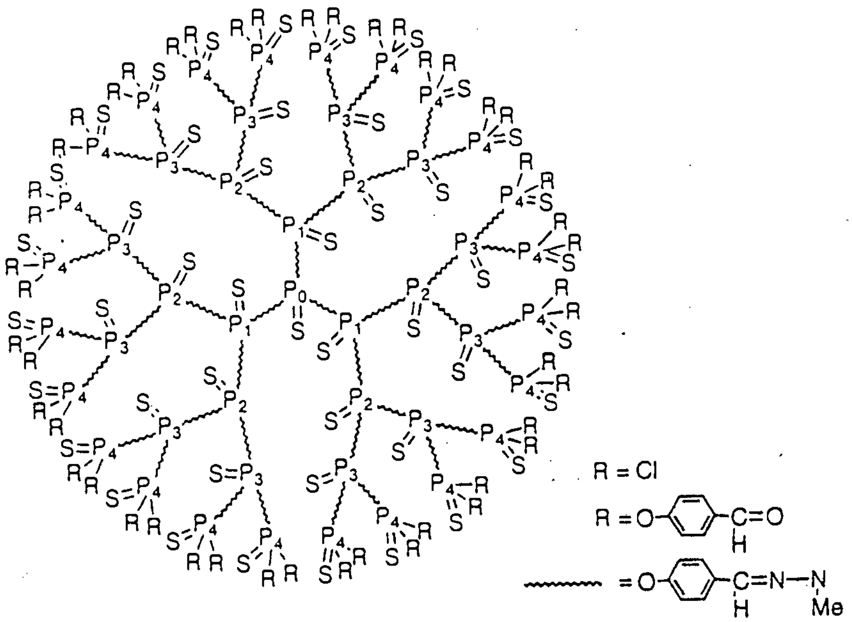
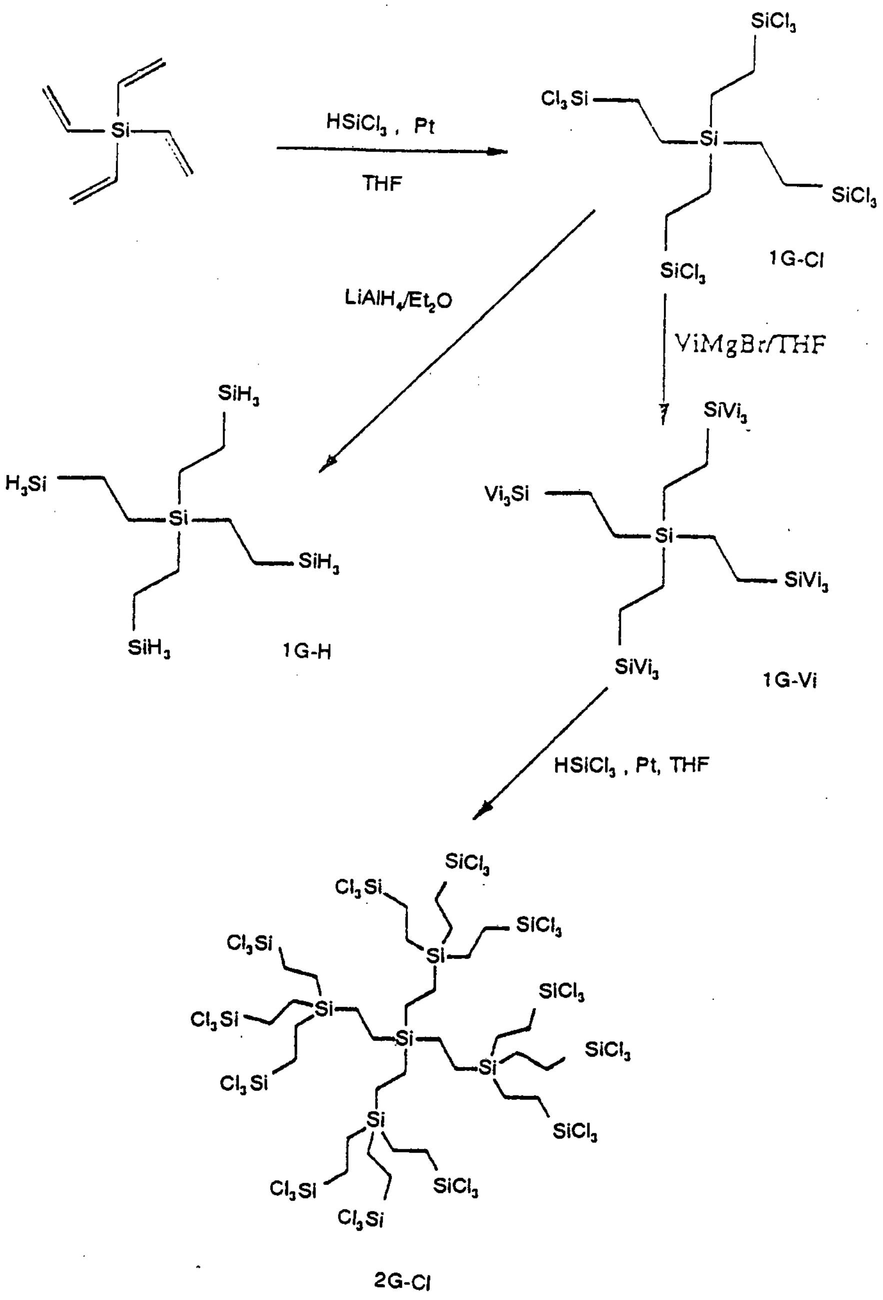


Figure 1.11 A fourth generation neutral phosphorus dendrimer[62]

In 1994, Seyferth and co - workers reported novel organosilicon dendrimers containing 324 Si-H bonds.[63] They adopted the divergent approach based on tetravinylsilane as the core molecule and hydrosilylation (with $HSiCl_3$) and vinylation (with CH_2=CHMgBr) as the growth step, as shown in Scheme 1.6. The chlorosilane of each generation was reduced with $LiAlH_4$ to the corresponding silicon hydride. The final product was a fourth-generation carbosilane dendrimer containing 324 Si-H bonds on its periphery, see Figure 1.12. Pyrolysis studies show the third and the fourth generation hydrides are useful preceramic materials, but in view of the preparative procedure required, in practice, their utility is rather low.



Vi=vinyl

Scheme 1.6 The synthesis of a second generation carbosilane dendrimer[63]

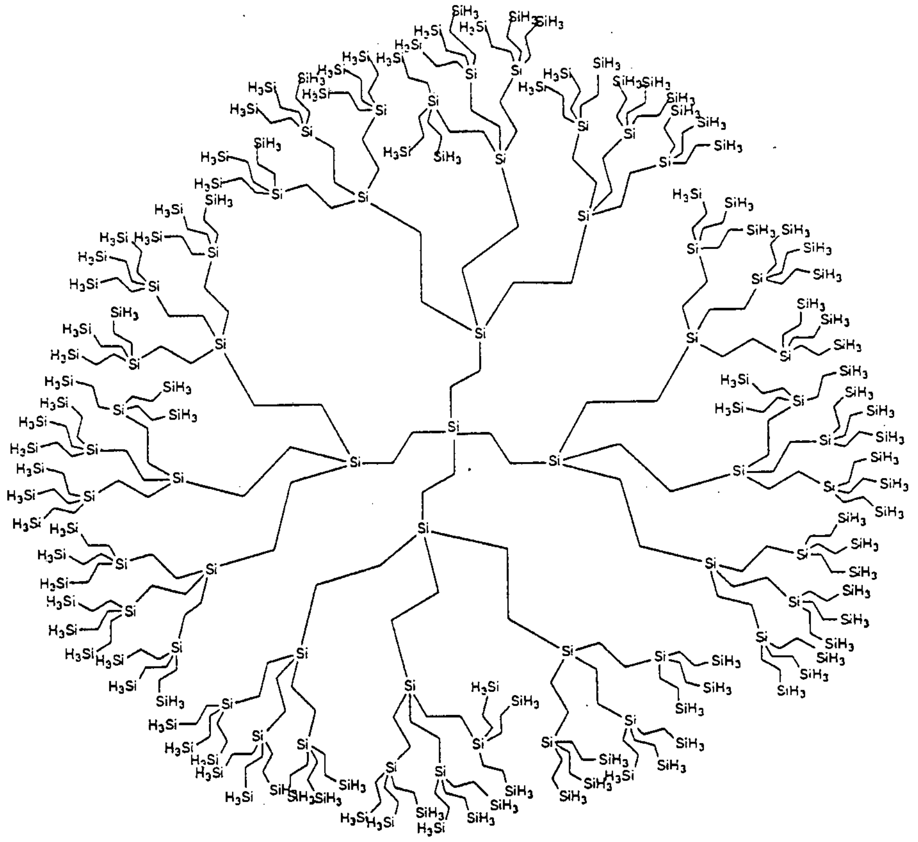


Figure 1.12 A fourth generation carbosilane dendrimer[63]

In 1995, Lambert and co - workers reported the first polysilane dendrimer.[64] This polysilane dendrimer containing 16-silicon atoms was constructed by the divergent approach, in which the largest silane chain of seven silicon atoms is repeated 27 times. The structure of this polysilane dendrimer is shown in Figure 1.13. Si-Si bonds tend to be labile, but the rupture of one or two peripheral Si-Si bonds in this molecule would still leave many Si_7 pathways intact, thus preserving the electronic and optical properties that make this polysilane important. In addition, the dendritic architecture is expected to make the inner Si-Si bonds less accessible to reagents and therefore more stable.

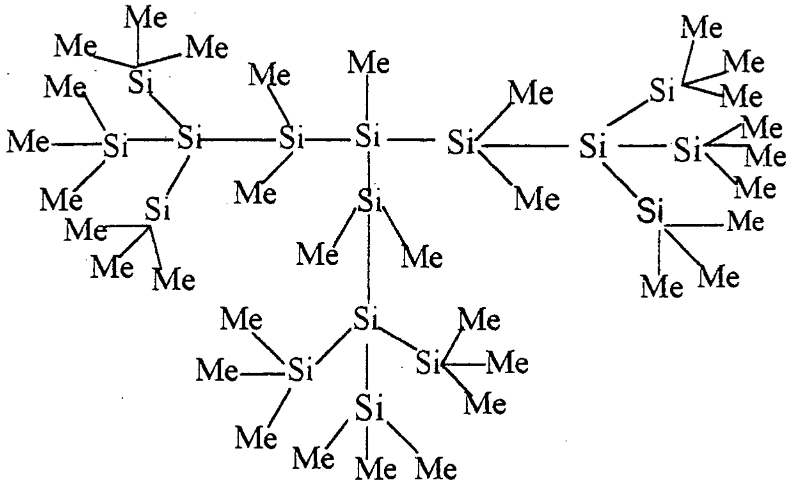
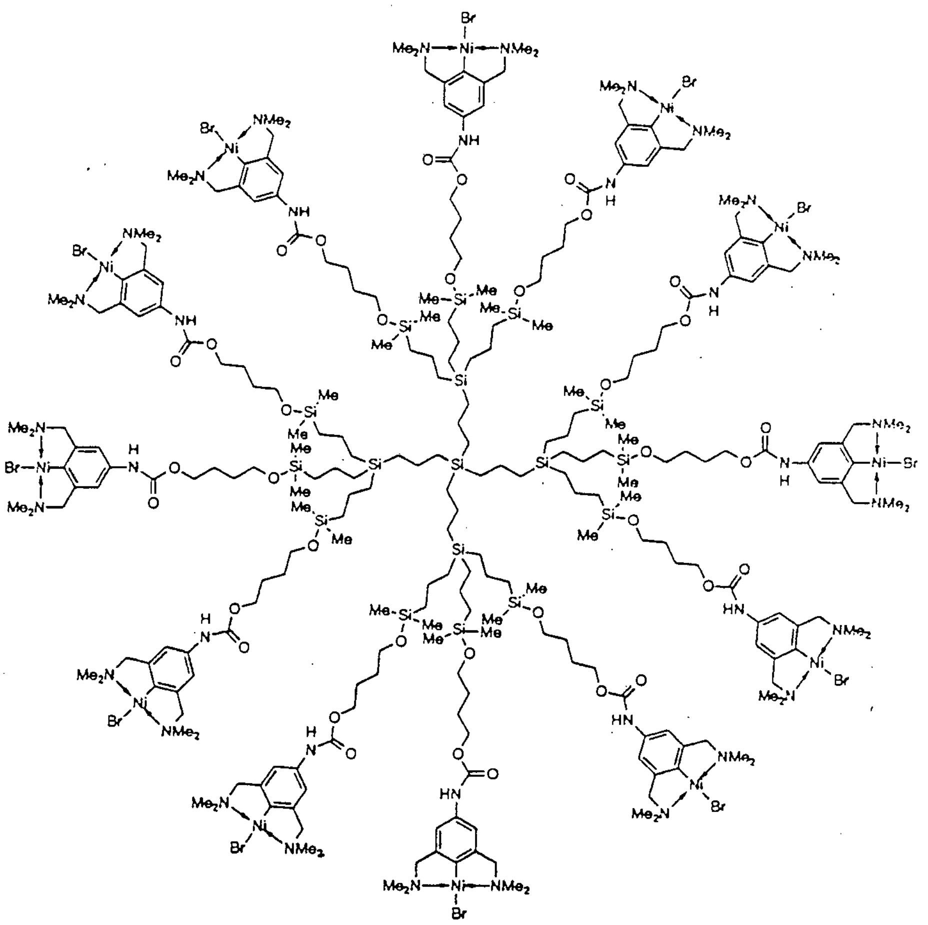


Figure 1.13 A structure of polysilane dendrimer[64]

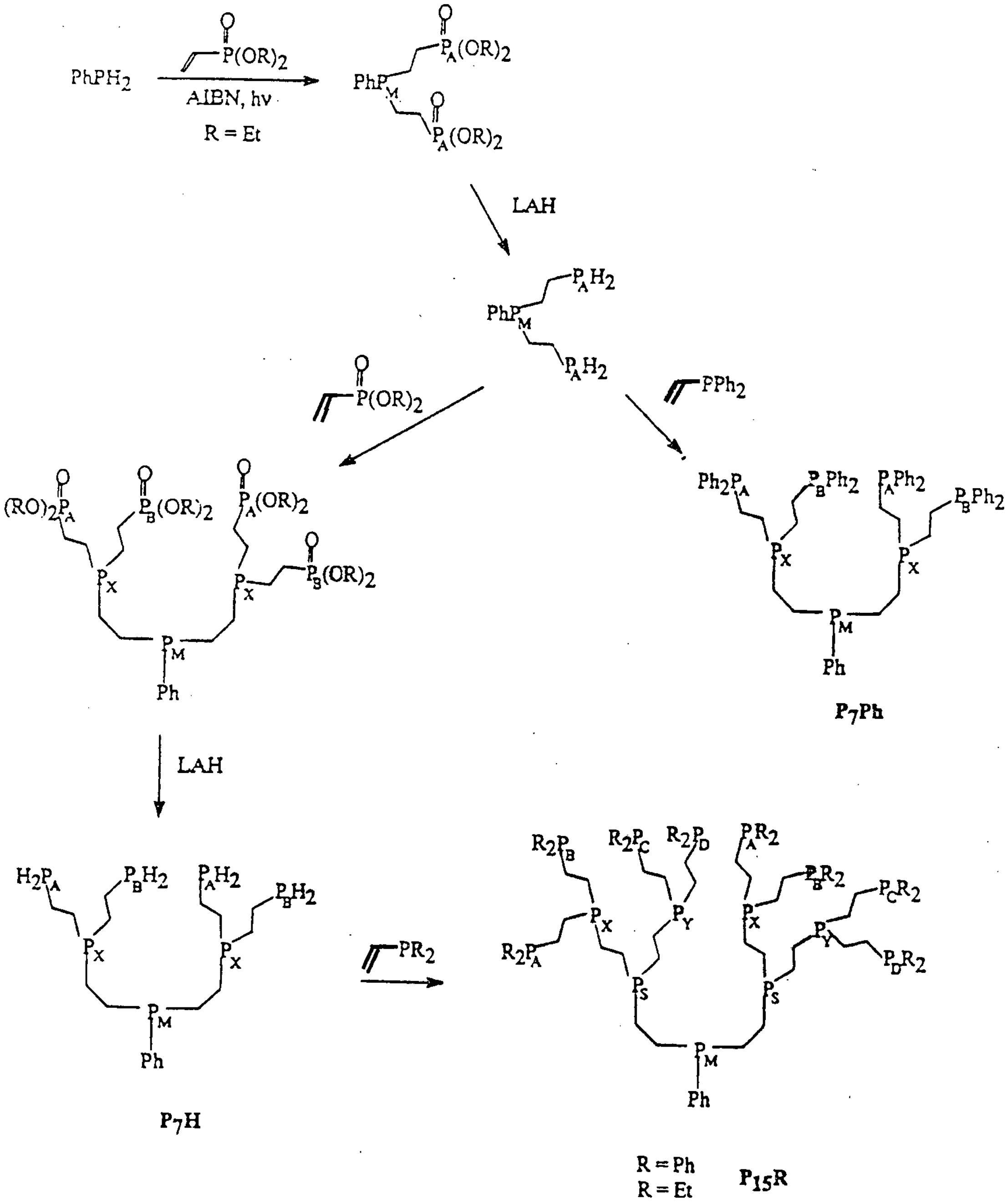
In 1994, Gerard van Koten and co - workers reported the first dendrimer-supported homogeneous catalysts.[30] The catalysts are polysilane dendrimers functionalized on the periphery with catalytically active arylnickel(II) complexes. The divergent methodology is employed in the synthesis. A polysilane dendrimer functionalized with 12 diamino arylnickel(II) complexes is shown in Figure 1.14 . These catalysts are effective in catalyzing the Kharasch addition of polyhalogenalkanes to olefinic double bonds. Unlike related catalyst systems anchored to soluble polymer supports, the new dendritic catalysts have physical characteristics such as size, solubility and dispersity of catalytic sites that are precisely defined, affording these dendrimers advantageous properties for physical seperation and catalyst recycling. Also, these dendritic catalysts retain the benefits of homogeneous catalysts, such as fast kinetics and accessibility of the metal sites.



Me = CH_3

Figure 1.14 Polysilane dendrimer containing 12 diaminoaryl complexes[30]

In 1994, DuBois and co-workers reported another class of interesting organophosphine dendrimers containing up to 15 phosphorus atoms.[65] The synthesis of the P_{15} dendrimer is shown in Scheme 1.7. The two main reactions used are the free radical addition of diethyl vinylphosphonate to a primary phosphine and the subsequent reduction of the resulting phosphonate with lithium aluminum hydride (LAH). These dendrimers react with $[Pd(CH_3CN)_4](BF_4)_2$ to produce metalated dendrimers which exhibit catalytic activity for the electrochemical reduction of CO_2 to CO. This is only the second example of dendrimer-supported catalysts ever reported. The structure of one of the metalated dendrimers is shown in Figure 1.15. This novel dendrimer contains five square planar metal centers, each with an inner coordination sphere composed of a triphosphine ligand and an acetonitrile ligand.



Scheme 1.7 The synthesis of the P_{15} dendrimer[65]

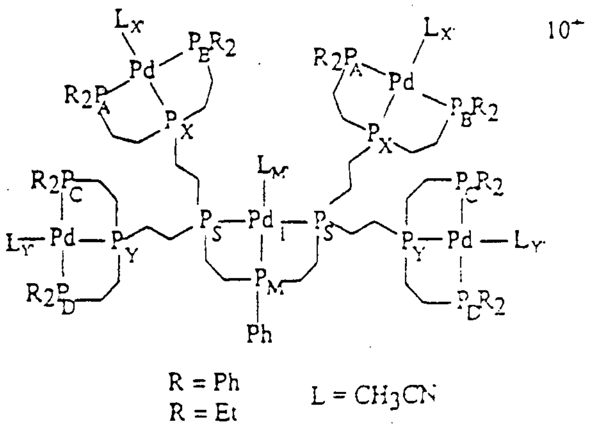


Figure 1.15 A metalated P_{15} dendrimer[65]

In 1994, Achar and Puddephatt reported a series of organoplatinum dendrimers synthesized by convergent methodology.[66] The largest organoplatinum dendrimer containing 28 platinum atoms, as shown in Figure 1.16, was obtained by reacting a dendritic wedge containing 7 platinum atoms with a tetra-functional core molecule. The characteristic feature of these dendrimers is that the transition metals are contained in every layer of the molecule except in the core.

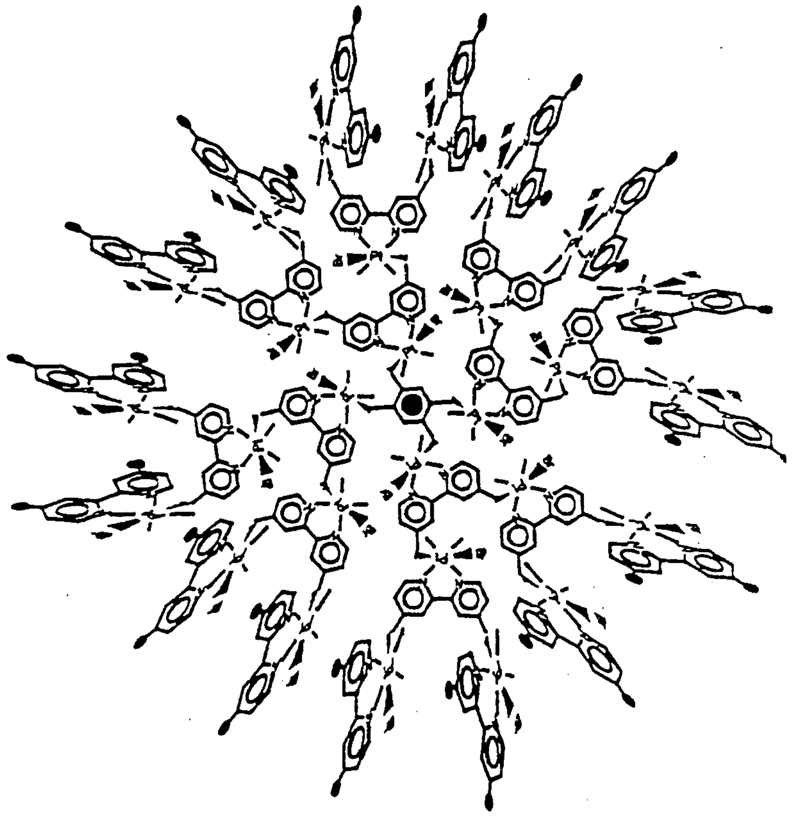
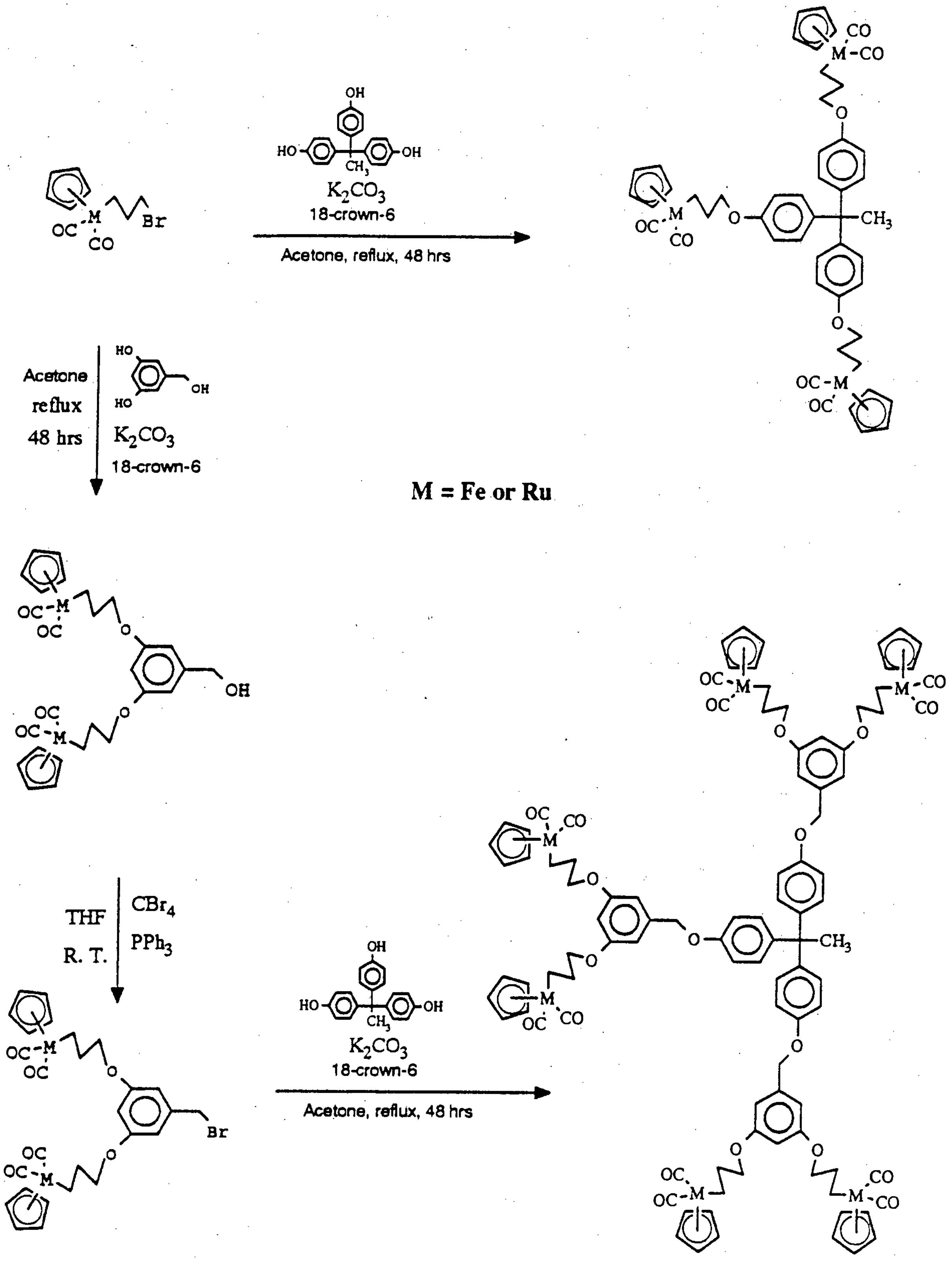


Figure 1.16 An organoplatinum dendrimer containing 28 Pt atoms[66]

In 1993, Liao and Moss reported the first series of organotransition metal dendrimers that contain metal-carbon σ bonds on the periphery of the molecules.[8] Up to second generation dendrimers containing 12 organoruthenium functional groups, ($CpRu(CO)_2CH_2CH_2CH_2$-) were synthesized by the convergent approach. The synthetic scheme for first generation is as shown in Scheme 1.8.

More recently, Liao and Moss have extended this synthetic methodology and prepared a very large organoruthenium dendrimer containing 48 organoruthenium groups which are located exclusively on the periphery of the dendritic structure.[51] This complex was obtained by reaction of a fourth generation dendritic wedge with a trifunctional core,1,1,1,-tris(4-hydroxyphenyl)ethane; has a nominal molecular mass of 18,438 amu and is believed to be the largest organotransition metal complex ever reported. The structure of a fourth generation dendritic wedge is shown in Figure 1.7

Currently, Moss and co-workers are exploring other organotransition metal dendrimers, including those containing iron (see Figure 1.17), tungsten, as well as heterobimetallic dendrimers.[67]



Scheme 1.8 The synthetic scheme for organometallic dendrimers[8]

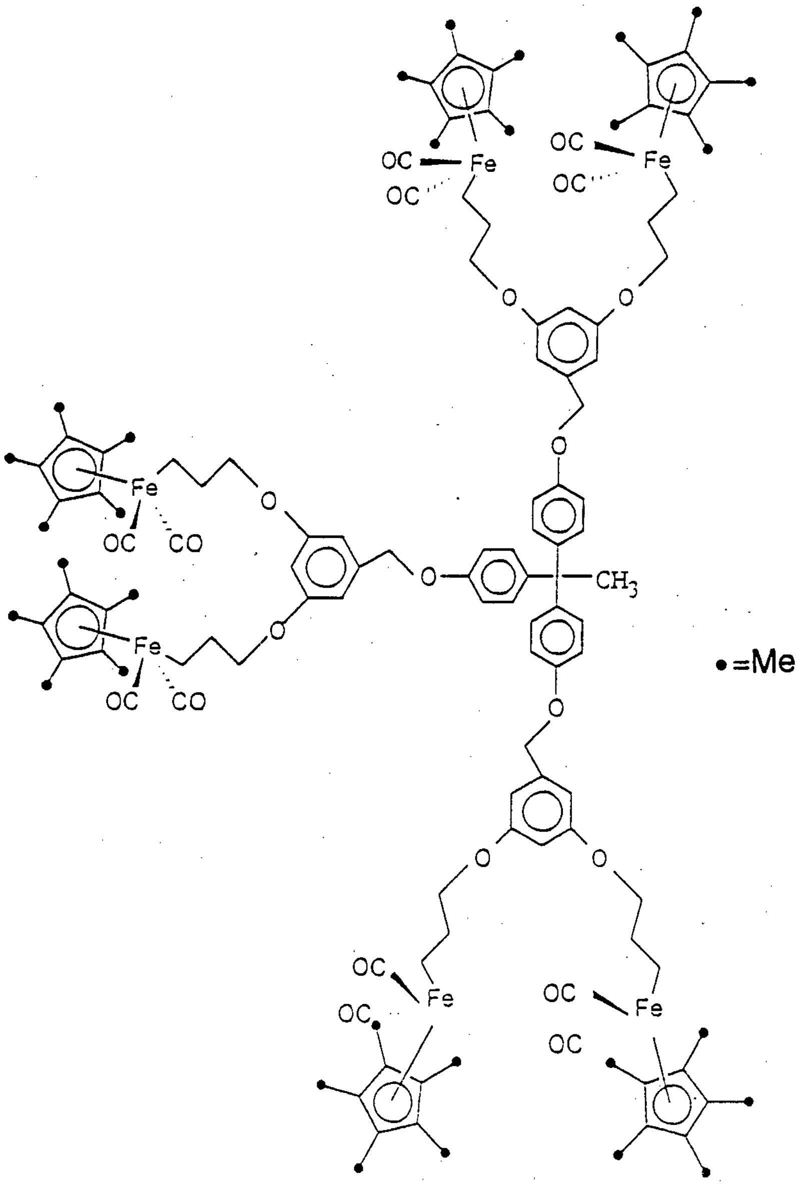


Figure 1.17 A first generation iron dendrimer[67]

1.4 Conclusion

Highly branched polymers called dendrimers are attracting a great deal of attention at the present time. They have potential specialized applications for example in drug delivery systems and as catalyst supports.

Dendrimers are prepared by stepwise growth methodology , which may be divergent methodology (growth from the center outwards) or convergent methodology (growth from outwards to the center).

Inorganic dendrimers which contain main group elements, or transition metals are currently of interest. Such as organoruthenium dendrimers, organoplatinum dendrimers, phosphorus dendrimers, carbosilane dendrimers, as well as polysilane dendrimers have been reported.

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Chapter 2 The synthesis, characterization and properties of novel block copolymers consisting of organoruthenium dendritic wedges and linear polyethylene glycol blocks

2.1 Introduction

Highly branched dendrimers are of considerable current interest. Because of their dense, but non-entangled structure, dendrimers are expected to impart unusual properties to other polymeric materials when incorporated into the polymer chain. Therefore, the study of linear dendritic block copolymers has attracted a great deal of attention recently.[1-6] The first organic linear-dendritic block copolymers were reported by Fréchet and coworkers in 1991.[1] These block copolymers contain both flexible (linear polyethylene glycols) and more rigid (dendritic) blocks and are able to form mono- and multimolecular micelles depending on the dendrimer generation and the concentration in methanol/water (a good solvent for linear blocks). Only monomolecular micelles are obtained in THF (a good solvent for the dendritic blocks).[3]

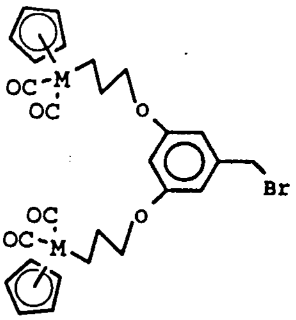
Polyethylene glycols (PEGs) and their derivatives are versatile polymers which have many applications such as phase-transfer reagents,[7] as compounds that could potentially encapsulate other materials,[8] and as emulsifying agents.[9] Organotransition metal dendrimers are new types of dendrimers,[10] and incorporation of them into polyethylene glycols (PEGs) will give novel materials which contain both organic and inorganic blocks. These new materials may have unusual or improved properties.

In this chapter we describe the synthesis of the first novel block copolymers containing organoruthenium dendritic wedges and polyethylene glycol blocks, their characterization by standard methods such as IR, NMR, SEC and elemental analysis, and discuss the properties of the resulting copolymers. In addition, the SEC results of some very large organoruthenium dendrimers are discussed.

2.2 Results and discussion

2.2.1 The synthesis of the first novel ABA type of block copolymers consisting of organoruthenium dendritic wedges and linear polyethylene glycol blocks

In this chapter, we describe the syntheses of two new ABA type of block copolymers containing organoruthenium dendritic wedges (A) and linear PEG (B) blocks. To the best of our knowledge, no block copolymers containing organometallic dendritic blocks have been reported. The dendritic wedge employed in the synthesis is a first generation organoruthenium dendritic benzyl bromide, namely Rp3G1Br, as shown in Figure 2.1.

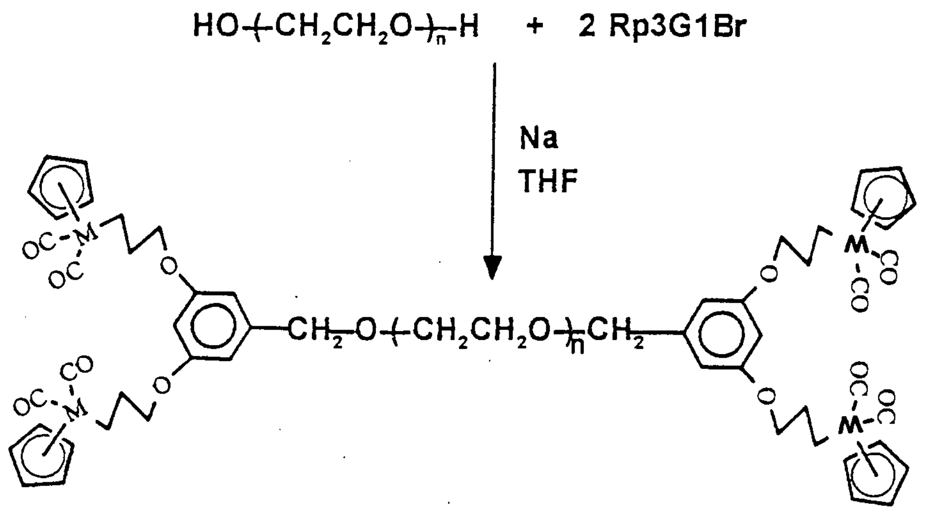


M = Ru

Figure 2.1 The structure of Rp3G1Br

The new block copolymers were prepared by capping the ends of α,ω-bifunctional PEGs, with dendritic wedges possessing a reactive functional group at their focal point. The synthetic scheme is shown in Scheme 2.1. In order to avoid the association of acidic moieties with PEG[11] and the incomplete conversion[7] of some Williamson-type syntheses, the formation of the PEG dianion in situ by reaction with NaH was carried out in the presence of the dendritic bromide. Two molar equivalents of dendritic bromide Rp3G1Br were reacted with one molar equivalent of PEG2,000

(average MW = 2,000, n = 45) or PEG10,000 (average MW = 10,000, n = 227) in the presence of NaH at 50°C. The reaction was monitored by TLC, eluting with a CH_2Cl_2/hexane (3:8) solution. The length of the PEG block influences the rate of formation of the copolymer - the longer the PEG blocks, the slower the rate. The resulting copolymers (3) and (4), as shown in Scheme 2.1, were purified by precipitation from acetone/methanol (1:3) and reprecipitation from THF/hexane to give reasonable yields of about 60%. In our experience, vigorous stirring throughtout the reaction is essential in order to have high conversion to product. Copolymers (3) and (4) are obtained as light brown powders and are relatively air stable.



M = Ru

(3) n = 45

(4) n = 227

Scheme 2.1 The synthetic scheme for block copolymers (3) and (4)

2.2.2 Characterization

2.2.2.1 IR spectroscopy

The IR spectra of block copolymers (3) and (4) were recorded in a CH_2Cl_2 solution. Both block copolymers showed two strong absorption bands at 2012 and 1947cm^{-1} corresponding to υ(CO) absorption bands, which are in the same positions as for the starting dendritic bromide Rp3G1Br.

2.2.2.2 ^{1}H and ^{13}C NMR spectroscopy

The block copolymers (3) and (4) were characterized by ^{1}H and ^{13}C NMR spectroscopy. A 200 MHz ^{1}H NMR spectrum of block copolymer (3) is shown in Figure 2.2. In all cases, the organoruthenium functional groups on the periphery of the dendritic block give four sets of resonances at positions: δ5.23 (Cp), 3.82 (CH_2O), 2.01 (CH_2), and 1.67 ($RuCH_2$) ppm. The resonances of the aromatic protons of the dendritic blocks occur in the region δ6.3-6.7ppm, almost exactly at the same position as for the dendritic bromide, Rp3G1Br. This can be seen in the ^{1}H NMR spectrum of the dendritic bromide, Rp3G1Br, in Figure 2.3. The strong and broad peak of δ3.61ppm in Figure 2.2 corresponds to the resonance of protons of the PEG block. The resonance at δ4.45ppm is assigned to the benzyl CH_2 protons. The integration of Cp to OCH_2CH_2O protons in the ^{1}H NMR spectrum of copolymer (3) is found to be 1:18.5. This is different to the expected result for compound (3) which should be 1:9 and is almost the same as the expected result, if only one dendritic wedge has been incorporated at one end of the PEG. We believe the synthetic method we have used should give a product which has a dendritic wedges at each end of PEG because 1.) two molar equivalents of dendritic wedges were used for one molar equivalent of PEG. 2.) the reaction mixture was stirred vigorously and 3.) this synthetic method is analogous to that used by Fréchet et al[2] in which two organic dendritic wedges have been incorporated with PEG. We believe that the difference in the integration of Cp to OCH_2CH_2O protons between the experimental and expected result is due to the compound (3) being contaminated by PEG. Similarly, from the integration of Cp to OCH_2CH_2O protons in compound (4) , we believe that this compound is also contaminated with PEG (expected ratio Cp to OCH_2CH_2O is 1:46 and found is1:77).

^{13}C NMR spectroscopy was found to be a useful tool for the confirmation of the formation of block copolymers. The resonances due to the benzyl CH_2 groups are clearly distinguishable from the other groups, such as CH_2OR, and CH_2Br. The resonance of the benzyl CH_2 of the starting material, Rp3G1Br is at ca.34ppm, as seen in the ^{13}C NMR spectrum of the dendritic bromide, Rp3G1Br, in Figure 2.5, however, the resonance of the benzyl CH_2 of the block copolymer is at ca.62ppm, as seen in the ^{13}C NMR spectrum of block copolymer in Figure 2.4.

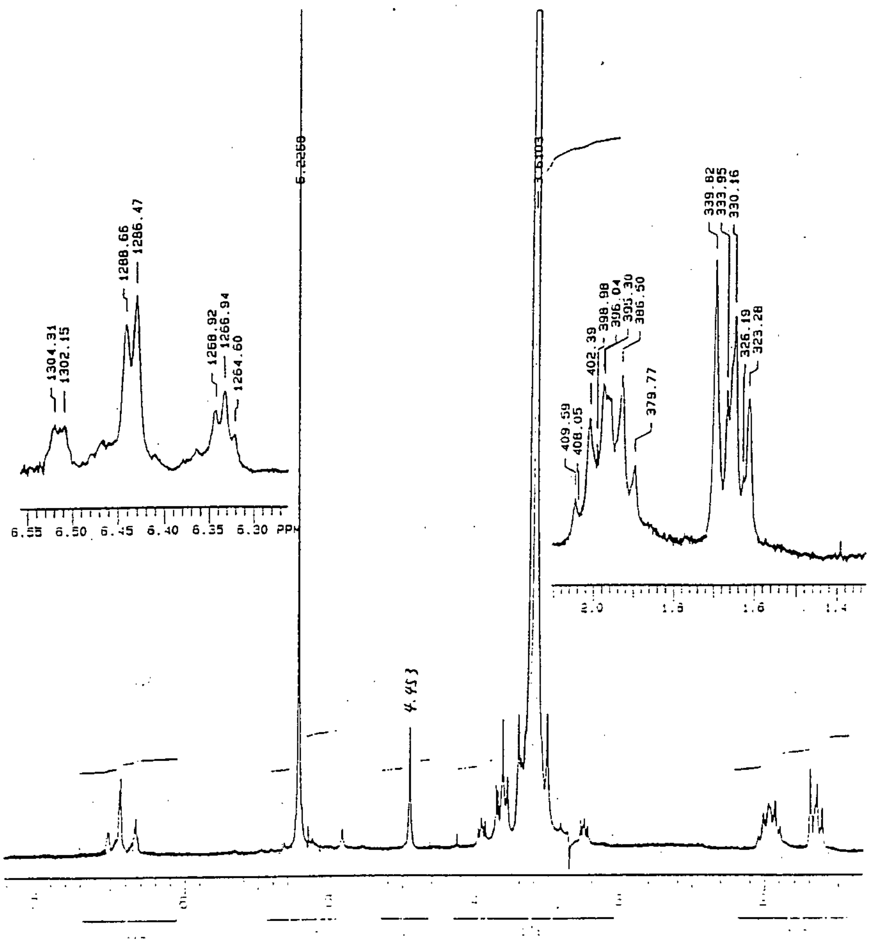


Figure 2.2 A ^1H NMR spectrum of block copolymer (3)

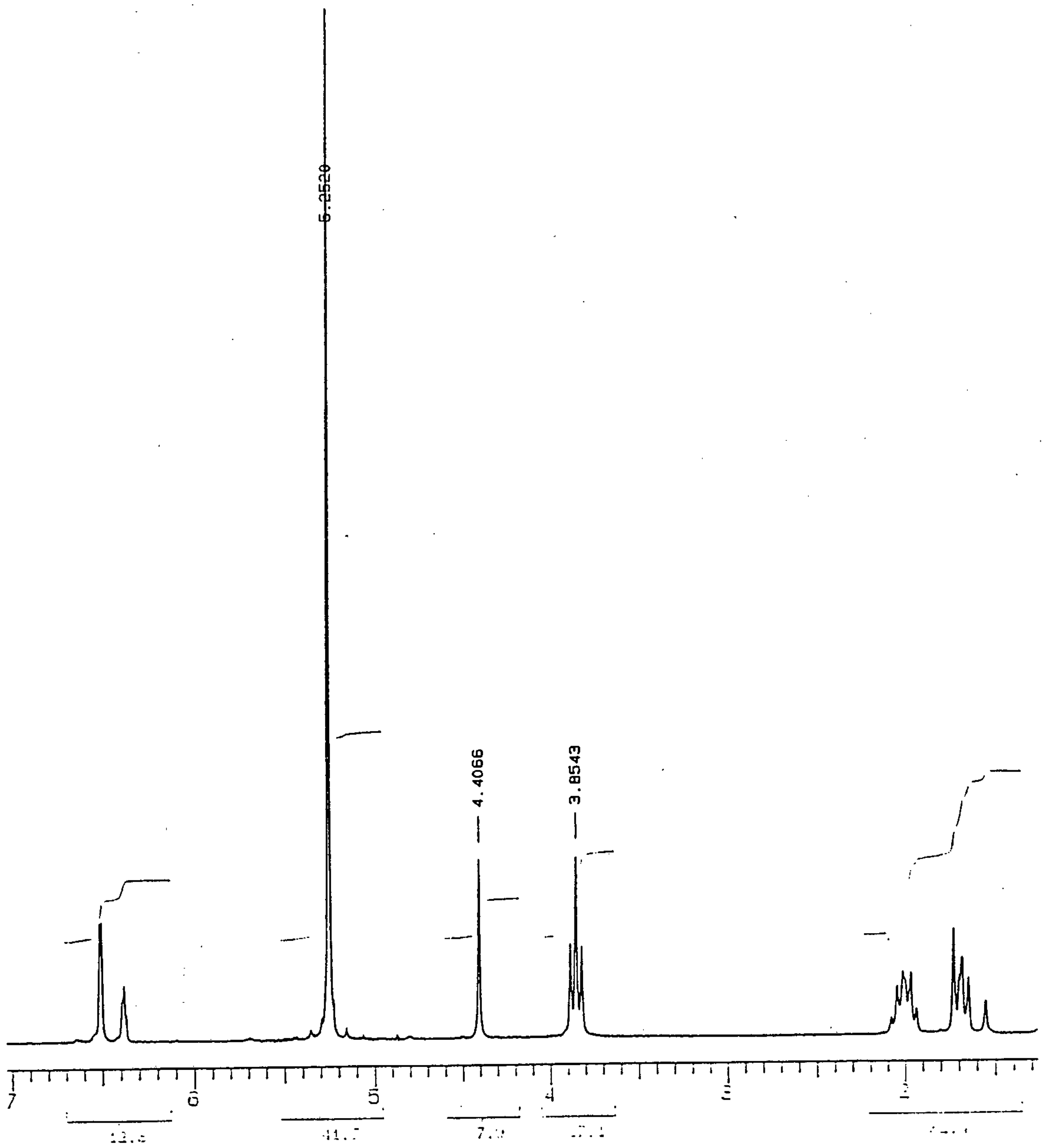


Figure 2.3 A ^1H NMR spectrum of Rp3G1Br

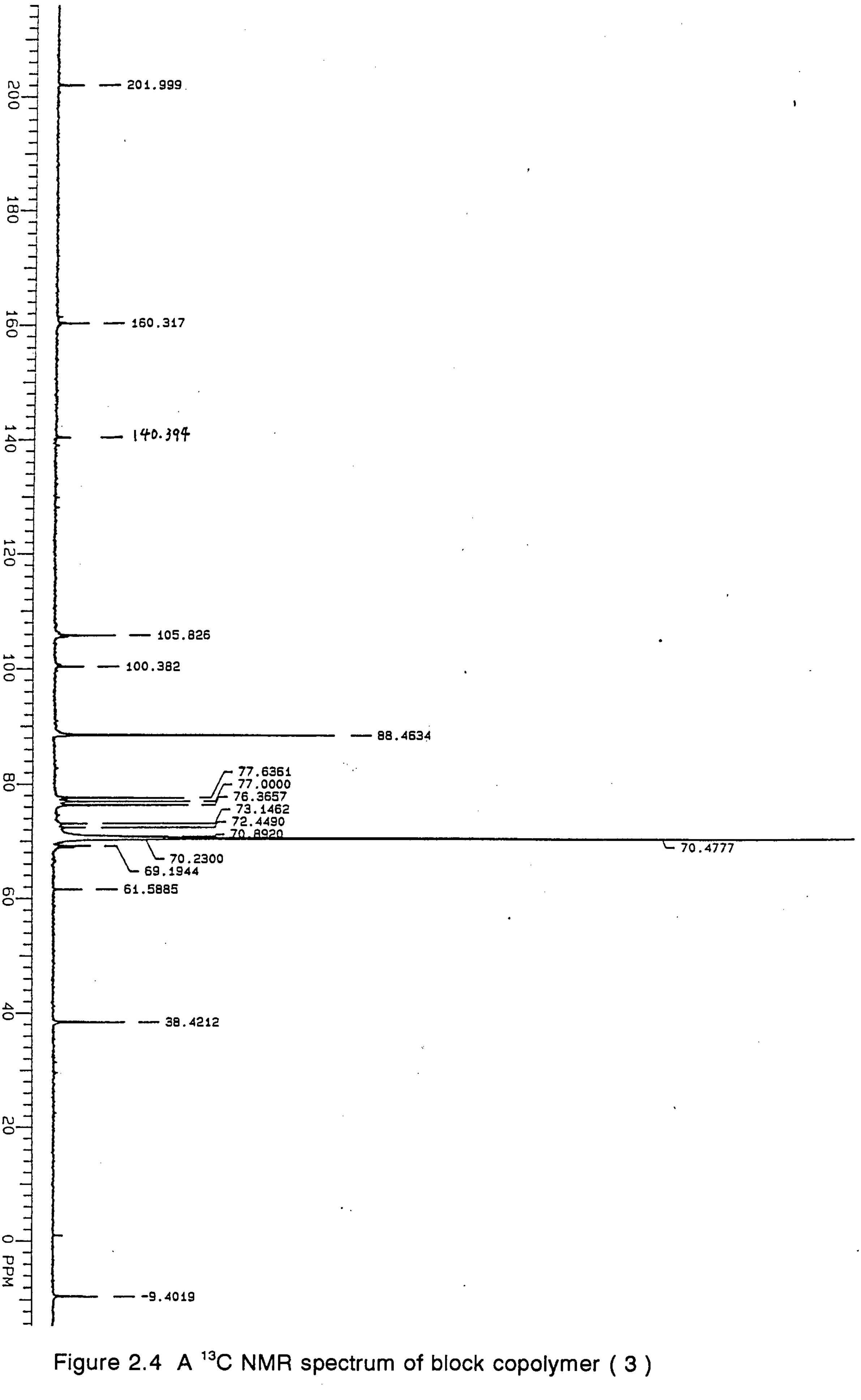


Figure 2.4 A ^{13}C NMR spectrum of block copolymer (3)

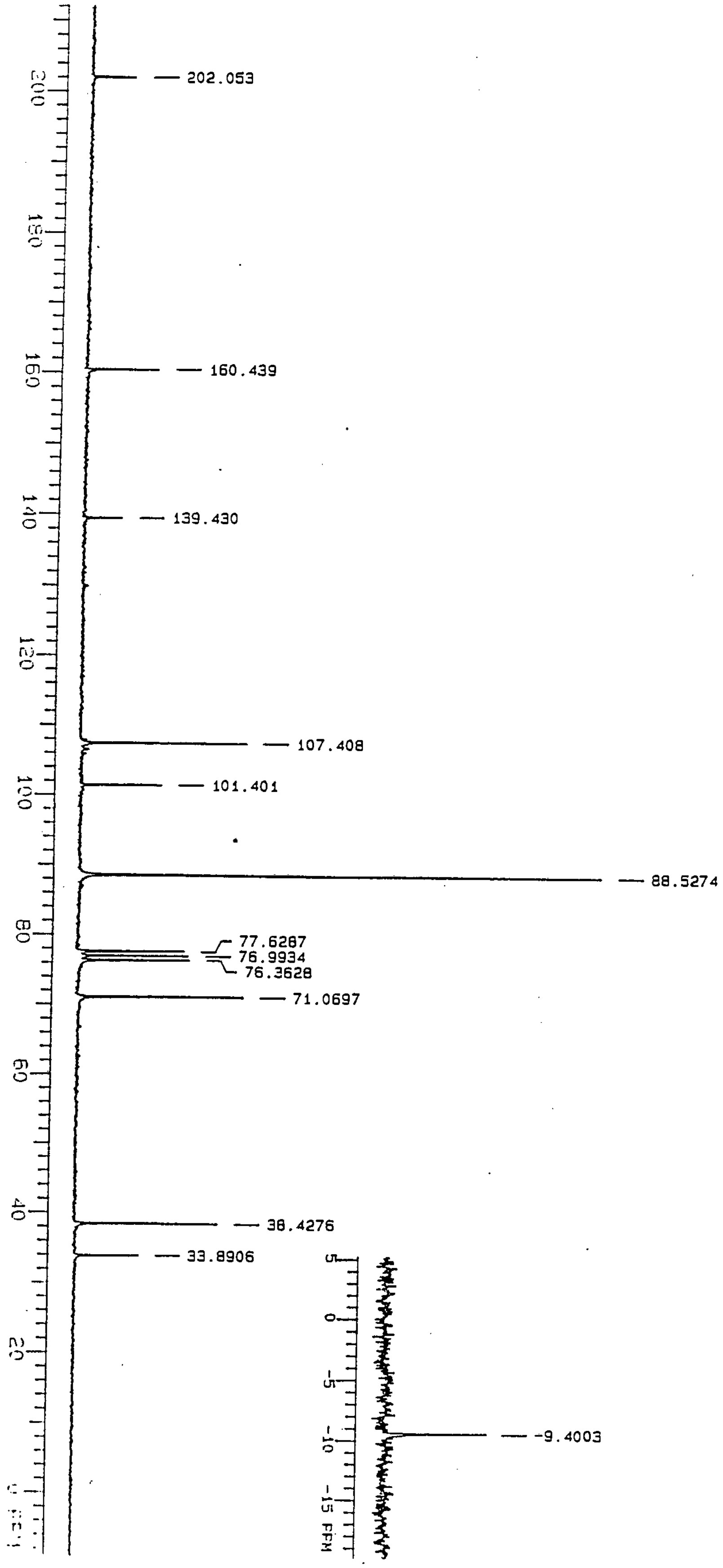


Figure 2.5 A ^{13}C NMR spectrum of Rp3G1Br

2.2.2.3 Elemental analysis

Elemental analysis results (C, H), are reasonable. The accuracy is affected by the polydipersive PEG block. The polydispersity index (PDI) of PEGs used in this synthesis is 1.41. Thus, ca.1% difference between calculated and experimental percentage carbon is reasonable.

2.2.2.4 Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) proved to be an extremely convenient method for checking the molecular mass and molecular weight distribution of the macromolecules. Here, we tested four samples : (i) a first generation ruthenium dendrimer, Rp3G1C;[12] (ii) a fourth generation ruthenium dendritic wedge, Rp3G4OH;[13] (iii) block copolymer (3); (iv) block copolymer (4). The relation between the molecular mass and the retention volume was calibrated by using monodispersed polystyrenes. The curves of calibration and elution for Rp3G1C and block copolymer (4) are shown in Figure 2.6 and 2.7. The SEC data is shown in Table 2.1.

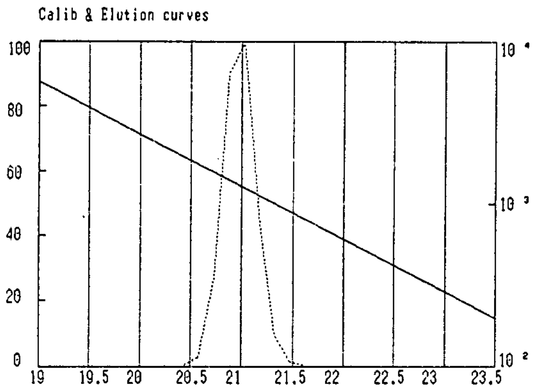


Figure 2.6 Calibration and elution curves for Rp3G1C

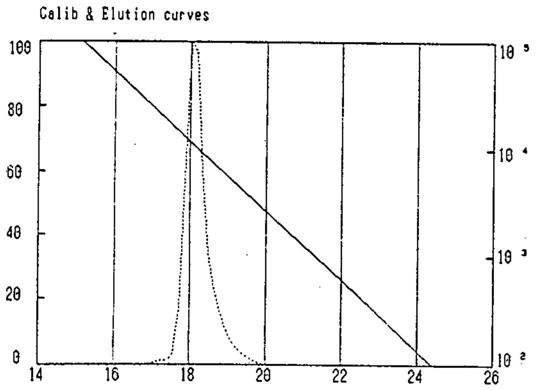


Figure 2.7 Calibration and elution curves for block copolymer (4)

Table 2.1 Size exclusion chromatographic data for block copolymers and organoruthenium dendrimers

Compound	Nominal MW	SEC data		
		Mw[a]	Mn[b]	PDI[c] = Mw/Mn
Rp3G1C	2252	1299	1281	1.01
Rp3G4OH	6062	2289	2208	1.04
Block copolymer (3)	3298	2372	2294	1.03
Block copolymer (4)	11298	10352	9583	1.08

([a]Mw i.e.weight average molecular weight, [b]Mn i. e. number average molecular weight, [c]PDI i.e. polydispersity index)

The stepwise synthesis of dendritic macromolecules Rp3G1C and Rp3G4OH should afford a monodispersed macromolecule i.e. a unimolecular compound. So far, due to the limitation of instruments in our laboratory, we were only able to obtain molecular weights up to about 4,500 by mass spectroscopy (FAB or EI). The molecular mass of a larger dendrimers, such as Rp3G4OH, is unable to be confirmed by mass spectroscopy , but can be estimated by SEC. It is interesting that the molecular masses estimated by SEC were always lower than the nominal molecular masses: 1299 for Rp3G1C (nominal mass 2252, confirmed by mass spectrum), and 2289 for Rp3G4OH (nominal mass 6062). A similar phenomenon has previously been reported by Hawker and Fréchet,[14] whose larger dendrimer with nominal mass of 40689 only shows a SEC result Mw of 15400. This indicates that such highly branched macromolecules have a globular polymeric structure which tends to be more strongly trapped in the gel phase, whereas polystyrenes used for standardization are linear macromolecules which should be linearly extended in solvents such as THF.[15] Polydispersity (PDI) data given in Table 2.1 suggest that that these dendritic macromolecules have a monodispersed nature (within experimental error).

The molecular masses of block copolymer (3) and (4) were estimated by SEC. It is interesting to note that our block copolymer (4) with a nominal molecular mass of 11298 shows a SEC polystyrene equivalent Mw of 10352. The smaller difference between the nominal molecular mass and SEC result indicates that this block copolymer has a similar conformation in THF solution as polystyrene and this is due to the major block of this block copolymer being linear PEG.

2.2.3 Properties

2.2.3.1 Thermal properties

Differential scanning calorimetry (DSC) was employed to obtain the melting points of these block copolymers. The data obtained are summarized in Table 2.2.

Table 2.2 Melting point of polymers and their block copolymers as determined by DSC

Polymer	PEG2,000	PEG10,000	Rp3G1Br	ABA type of block copolymer (3)	ABA type of block copolymer (4)
Melting Point (^{0}C)	54.16	63.44	107.83	47.67	58.14

The melting points of these block copolymers are lower than that of any pure block (A and B). This differs from other copolymers which have their melting points between that of pure blocks, and is probably due to the fact that the A block is only a first generation dendritic wedge. The mass of the A block is still small and can allow it to behave as a plasticizer to decrease the melting point of the matrix (i. e. B block).

The study of the degradation of polymers is of major interest since it can, in many cases, determine the upper temperature limit of use for the material. We used thermogravimetric analysis (TGA) to investigate the decomposition of these block copolymers. A typical TGA trace for these block copolymers is shown in Figure 2.8.

This curve shows two distinguishable weight loss steps: (i) From ca.159^{0}C to ca.333°C, a continuous weight loss (8.1%) is observed, corresponding to the decomposition of the organic groups of block A (calc.8.1%), i.e. the dendritic block. (ii) From ca.333°C to ca.470°C, a rapid weight loss (84.5%) takes place, corresponding to the decomposition of the PEG block (cal.88.4%). Thus, after the second decomposition step, ruthenium metal, or ruthenium oxide and small amount of carbon-rich material are left.

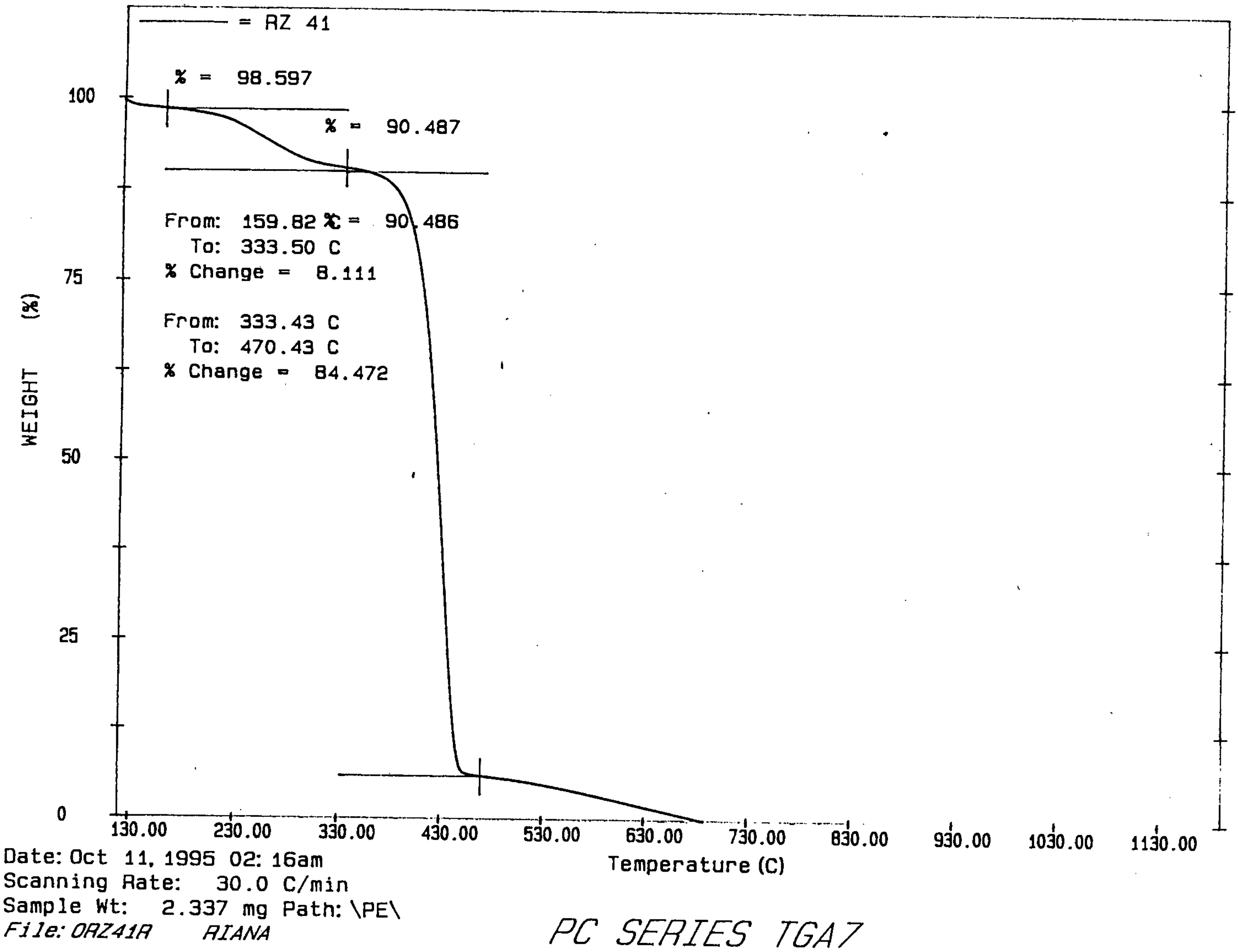


Figure 2.8 A TGA curve of block copolymer (4).

2.2.3.2 Morphology

These block copolymers dissolve in polar organic solvents, such as CH_2Cl_2 and THF. The solubility of these metal-containing copolymers may be the key to the preparation of thin films. Thus, the morphologies of these copolymers were studied.

Transmission electron microscopy (TEM) was employed to study the morphology of each block copolymers. Films of these block copolymers were prepared by allowing dichloromethane solutions to evaporate on a copper grid by a slow and continuous nitrogen stream over a period of 3-4 days.

TEM micrographs of these block copolymers are shown in Figures 2.9 and 2.10. Films exhibited either irregular spherical (Figure 2.9) morphology or regular spherical (Figure 2.10) morphology, depending on the weight percentage of the ruthenium-containing block. In the case of block copolymer (3) an irregular spherical structure was obtained. In block copolymer (4), a regular spherical morphology was obtained. These reveal that ruthenium-containing dendritic blocks in the block copolymers readily associate to yield microdomains because of the great disparity in the characteristics of the two blocks; one would not normally expect such a relatively small metal-containing block to induce microphase separation.[16]

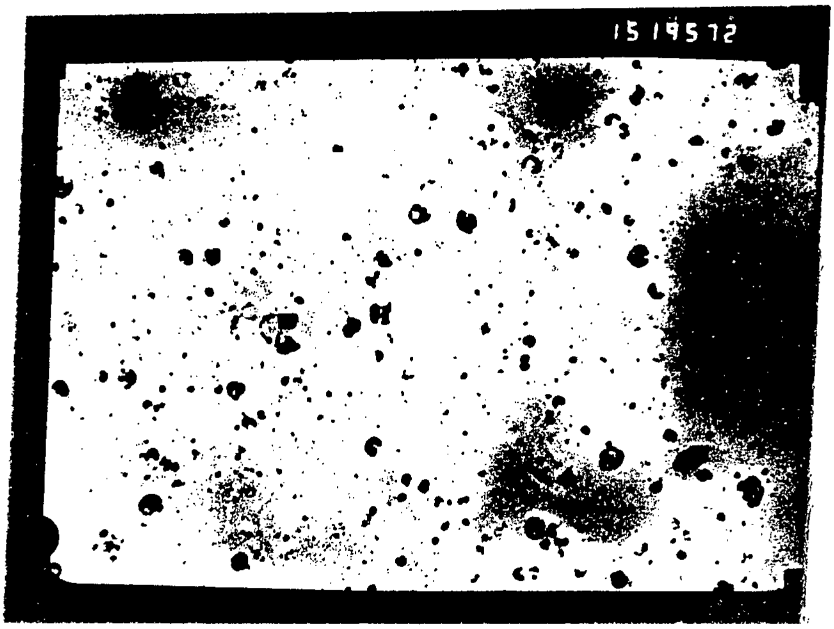


Figure 2.9 A TEM micrograph of block copolymer (3) (magnification 15,000)

Figure 2.10 A TEM micrograph of block copolymer (4) (magnification 7,300)

2.2.3.3 Preliminary thin metallic film study

Continuing interest in ruthenium thin films stems from their application as resistor pastes for miniaturised electronic circuits such as those used in mobile phones, satellite communications equipment and other compact, high quality electronic goods. Thermal treatment or chemical vapor deposition (CVD) represent two important routes for thin film preparation.[17] In this preliminary thin metallic film study, we employed the ruthenium-containing block copolymer (4) as a precursor for thin film deposition by thermal decomposition.

As we know from TGA, the block copolymer (4) decomposes and loses most of the organic groups by 500°C. Thus the thin block copolymer films, which were prepared by allowing dichloromethane solutions to evaporate on a copper grid by a slow and continuous nitrogen stream over a period of 3-4 days, were heated in oven at 500°C for 20 min. This resulted in the deposition of thin ruthenium films. A TEM micrograph of such a film (magnification 200) is shown in Figure 2.11

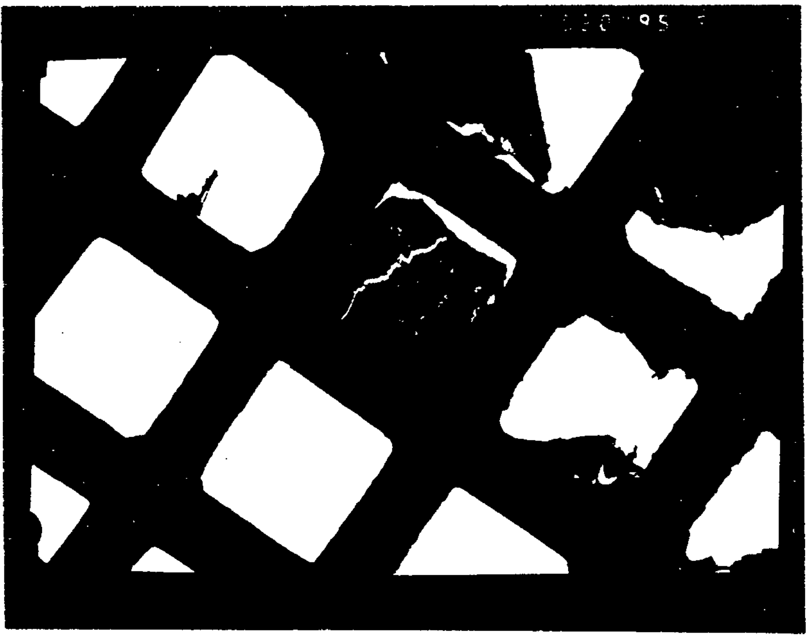


Figure 2.11 TEM micrograph of ruthenium films deposited from block copolymer (4) on heating to 500°C (magnification 200)

This micrograph reveals that thermal degradation of ruthenium-containing block copolymers may form thin ruthenium films, but the films are not completely smooth. This is probably because the percentage of ruthenium in this block copolymer is not high enough to deposit smooth films. We suggest higher generation ruthenium dendrimers, which contain a much higher percentage of ruthenium in the polymers, may form better quality ruthenium films.

The thin ruthenium films were observed in higher magnification, i.e. 10,000. The micrograph, as shown in Figure 2.12, reveals that well - dispersed ruthenium particles are formed. It may be possible to produce well - dispersed metal particles for use as heterogeneous catalysts by thermal degradation of these polymers.

Figure 2.12 TEM micrograph of ruthenium particles deposited from block copolymer (4) at 500°C (magnification 10,000)

2.3 Conclusion

The results obtained show that the novel linear organoruthenium dendritic block copolymers can be synthesized by an end-capping reaction. These copolymers dissolve in polar organic solvents, such as CH_2Cl_2 and THF and can be characterized by IR, NMR, SEC, as well as elemental analysis. The ruthenium-containing dendritic blocks in the block copolymers readily associate to yield microdomains. These block copolymers may be used as precursors for thin metal films by thermal decomposition, and may have potential application in the production of well - dispersed metal particles for use as heterogeneous catalysts.

We believe that the difference in ratio of integration of Cp to OCH_2CH_2O protons between the experimental and expected results for compounds (3) and (4) is due to the samples being contaminated by PEG. These compounds could be further purified by dissolving them in acetone and careful reprecipitation with methanol. Additional confirmation of the formulation of these copolymers could be obtained by the reaction of the dendritic wedges with high purity PEG of a known molecular weight. The molecular weight of the resulting copolymers could then be obtained by mass spectrometry and the number of dendritic wedges that had been incorporated to the PEG could be determined then with certainty.

2.4 Experimental

2.4.1 Methods

Melting points were obtained from differential scanning calorimetry (DSC). DSC was carried out on the Perkin Elmer PC Series DSC7 instrument. Samples were heated under nitrogen from -20°C to 150°C at a rate of 10°C/min.. The thermogravimetric analysis (TGA) was carried out on the Perkin Elmer Thermogravimetric Analyzer TGA7. Samples were heated under nitrogen at a rate of 30°C/min.. Transmission electron microscopy (TEM) was carried out at the Electron Microscopy Unit in University of Cape Town, and the results were obtained from a JEOL TEM-200CX microscope. Films of the block copolymers were prepared by allowing dichloromethane solutions to evaporate on a copper grid by a slow and continuous nitrogen stream over a period of 3-4 days. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer in solution cells with NaCl windows. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 200 or a Varian Unity 400 spectrometer. All NMR spectra were recorded in $CDCl_3$ solution. Chemical shifts are given in ppm. ^{1}H and ^{13}C NMR are referenced to internal tetramethylsilane (TMS) Size Exclusion Chromatography (SEC) was performed on a Shimadzu liquid chromatograph system consisting of a Shimadzu LC-6A pump, a Shimadzu RID-6A differential refractometer and a Shimadzu SPD-6Av UV spectrophotometric detector (at 254nm). THF at 40°C with nominal flow rate of 1ml/min. was used as the mobile phase. The separations were achieved across banks of two Shodex columns (KF-804 and KF-806m). The system was calibrated versus commercially available monodispersed polystyrene (PSt) standards.

2.4.2 Materials

PEGs (average molecular weight 2,000 and 10,000) and NaH were obtained from Aldrich Chemical Co. Ltd. The first generation organoruthenium dendritic wedge, Rp3G1Br, was prepared by literature methods.[12,18] THF was distilled over sodium wire and benzophenone under nitrogen. All the other solvents were reagent grade and used without further treatment, unless otherwise specified.

2.4.3 Preparation of block copolymers

All reactions were carried out under a nitrogen atmosphere using standard Schlenk tube techniques.

The preparation of block copolymer (3):

PEG of average molecular weight 2,000 [$H(OCH_2CH_2)_{45}OH$] (0.0850g, 0.0425mmol) and the ruthenium dendritic wedge Rp3G1Br (0.0637g, 0.0874mmol) were mixed and dissolved in dry THF (2ml). To the solution was added NaH (0.0030g, 0.12mmol), and the reaction mixture was stirred at 50°C for 6 hours under nitrogen. The reaction was monitored by TLC, eluting with a CH_2Cl_2/hexane (3:8) solution. After the reaction was judged complete, the reaction mixture was filtered and and the solvent was removed under reduced pressure. The residue was purified by dissolution in acetone and precipitation with methanol, and repurified by dissolution in THF and reprecipitation with hexane. Yield: 0.086g (61%). m.p.: 48°C;

IR (CH_2Cl_2) υ(CO): 2012s, 1947s cm^{-1};

^{1}H NMR δ ($CDCl_3$)ppm: 6.44 (d, J = 2Hz, 4H, Ar), 6.33 (t, J = 2Hz, 2H, Ar), 5.23 (s, 20H, Cp), 4.45 (s, 4H, $ArCH_2$), 3.82 (t, J = 7Hz, 8H, CH_2OAr), 3.61 (broad, 370H, OCH_2CH_2O), 2.01 (m, 8H, CH_2), 1.67 (m, 8H, $RuCH_2$);

^{13}C NMR δ ($CDCl_3$)ppm: 201.99 (CO), 160.32, 140.39, 105.83, 100.38 (Ar), 88.55 (Cp), 70.89 (CH_2OAr), 70.48 (OCH_2CH_2O), 61.59 ($ArCH_2$), 38.42 (CH_2), -9.40 ($RuCH_2$); Found C 51.42%, H 7.62%, Calc. for $C_{144}H_{234}O_{58}Ru_4$ (M = 3298) C 52.45%, H 7.15%.

The preparation of block copolymer (4):

PEG of average molecular weight 10,000 [$H(OCH_2CH_2)_{227}OH$] (0.430g,0.0430mmol) and the ruthenium dendritic wedge Rp3G1Br (0.0642g, 0.0880mmol) were mixed and dissolved in dry THF (4ml). To the solution was added NaH (0.0030g, 0.12mmol), and the reaction mixture was stirred at 50°C for 24 hours under nitrogen. The reaction was monitored by TLC, eluting with a CH_2Cl_2/hexane (3:8) solution. After the reaction was judged complete, the reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was purified by dissolution in acetone and precipitation with methanol, and repurified by dissolution in THF and reprecipitation with hexane. Yield: 0.293g (60%). m.p.: 58°C;

IR (CH_2Cl_2) υ(CO): 2012s, 1947s cm^{-1};

^1H NMR δ ($CDCl_3$)ppm: 6.45 (d, J = 2Hz, 4H, Ar), 6.35 (t, J = 2Hz, 2H, Ar), 5.24 (s, 20H, Cp), 4.47 (s, 4H, $ArCH_2$), 3.83 (t, J = 7Hz, 8H, CH_2OAr), 3.62 (broad, 1540H, OCH_2CH_2O), 2.01 (m, 8H, CH_2), 1.67 (m, 8H, $RuCH_2$);

^{13}C NMR δ ($CDCl_3$)ppm: 202.01 (CO), 160.40, 140.39, 105.92, 100.13 (Ar), 88.50 (Cp), 70.89 (CH_2OAr), 70.52 (OCH_2CH_2O), 61.44 ($ArCH_2$), 38.47 (CH_2), -9.36 ($RuCH_2$); Found C 52.53%, H 8.71%, Calc. for $C_{508}H_{962}O_{240}Ru_4$ (M = 11298) C 53.92%, H 8.57%.

2.5 References

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18. Y. H. Liao, PHD thesis, University of Cape Town, 1994.

Chapter 3 The synthesis, characterization, and potential application of novel ruthenium-containing dendritic phosphine metal complexes

3.1 Introduction

Industrial uses of homogeneous catalyst systems are increasing. Two very important factors to emerge from the study of these homogeneous systems are their reactivity and selectivity as compared with heterogeneous systems. It is not co-incidental that many homogeneous catalysts contain tertiary phosphine ligands. These ligands possess the correct steric and electronic properties that are necessary for catalytic reactivity and selectivity. One of the most important homogeneous catalysts is $[RhCl(PPh_3)_3]$, known as Wilkinson's catalyst, which catalyzes the hydrogenation of alkenes at 25°C under one atmosphere pressure of dihydrogen.[1,2] However, the major disadvantage of homogeneous catalysts is the problem of seperating the very expensive catalyst from the products at the end of the reaction. With heterogeneous catalysts, this can be achieved by some kind of coarse filtration whereas with homogeneous catalysts, a very efficient distillation or ion-exchange process is required. Ideally, one would prefer a heterogeneous catalyst with the reactivity and selectivity of a homogeneous catalyst. Therefore, studies of supported catalysts, which combine the advantages of homogeneous and heterogeneous catalysts - displaying high selectivity and reactivity in combination with ease of seperation from reaction mixture - attract both industrial and academic interest.[3]

Dendrimer supported catalysts are new types of supported catalysts. Up to now, only two successful examples have been reported.[4,5] The first dendrimer supported catalysts, which were reported by van Koten et al in 1994,[4] are polysilane dendrimers functionalized on the periphery with catalytically active arylnickel(II) complexes. These catalysts are effective in catalyzing the Kharasch addition of polyhalogenalkanes to olefinic double bonds.

The ruthenium dendrimers synthesized by our group contain ruthenium metal exclusively on the periphery of the macromolecular structure.[6,7] One potentially interesting modification is the conversion to dendritic phosphines. The dendritic phosphines may react with catalytically active metal complexes to give new dendrimer-supported complexes. Such dendrimer-supported metal complexes raise the possibility of combining the rich catalytic chemistry of transition metal phosphine complexes with highly structured macromolecular chemistry. Our initial efforts in this are the subject of this chapter.

In this chapter we describe the syntheses of the novel ruthenium-containing dendritic phosphine metal complexes, their characterization by standard methods such as IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and elemental analysis, and we also discuss the potential catalytic application of the dendritic phosphine platinum complexes in the hydroformylation reaction.

3.2 Results and discussion

In this study, the key step in synthesizing the dendritic phosphine metal complexes is the preparation of the dendritic phosphine ligands. The dendritic wedge empolyed in the synthesis of the ruthenium-containing dendritic phosphine ligand is a first generation organoruthenium dendritic benzyl bromide, namely Rp3G1Br, as shown in Figure 3.1.

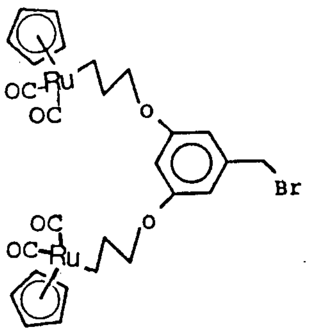


Figure 3.1 The structure of Rp3G1Br

The novel ruthenium-containing dendritic phosphine ligand (abbreviated as RDP), shown in Figure 3.2, was prepared by reaction of $LiPPh_2$ with Rp3G1Br in THF (eq. 1).

$$LiPPh_2 + Rp3G1Br \longrightarrow RDP + LiBr \qquad (1)$$

The resulting ruthenium-containing dendritic phosphine ligand is extreamly air sensitive and readily oxidized to the phosphine oxide during purification. Although the yield (83%) is good, the majority of product is ruthenium-containing dendritic phosphine oxide instead of phosphine. This can be seen in the ^{31}P NMR spectrum in Figure 3.3.

The strong peak of δ29.89ppm in Figure 3.3 corresponds to the phosphorus resonance of the phosphine oxide whereas the resonance of δ38.54ppm is assigned to the phosphorus of the phosphine.

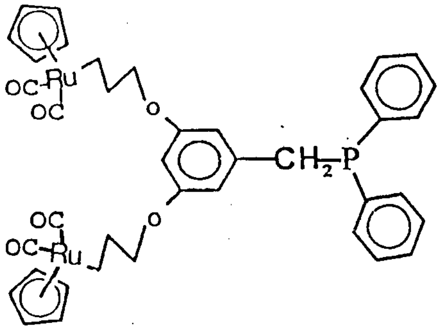


Figure 3.2 The structure of the ruthenium-containing dendritic phosphine, RDP

So far, due to equipment limitations in our laboratory, we are unable to isolate the pure RDP ligand, but the coordination of these RDP ligands to metal complexes can be carried out, in situ, without any further purification of the RDP ligands.

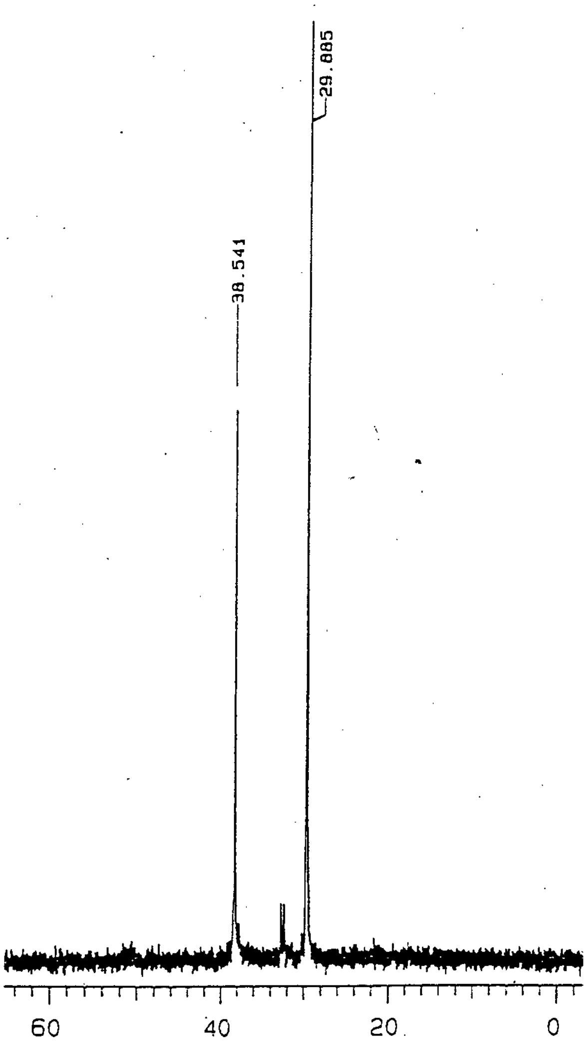


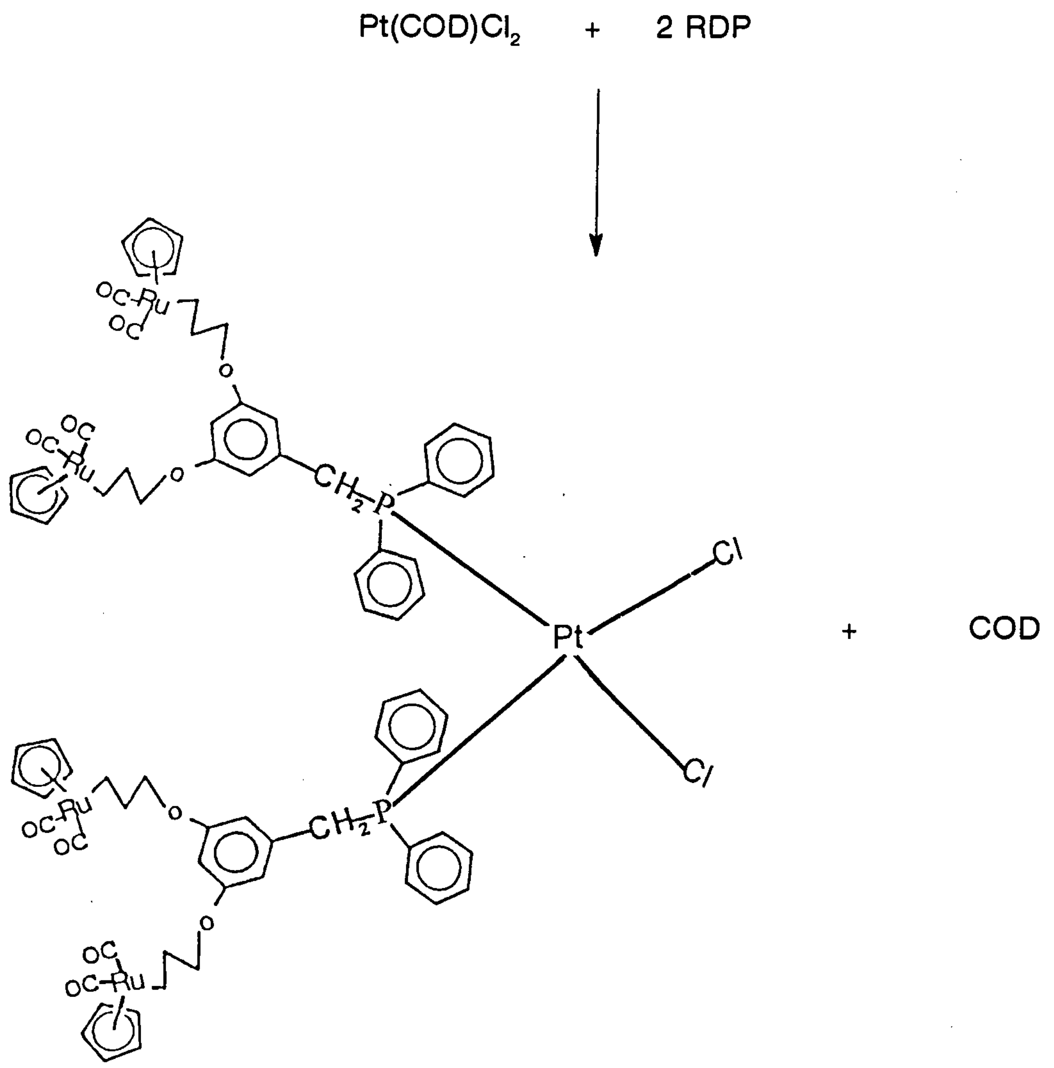
Figure 3.3 A ^{31}P NMR spectrum of RDP and its oxide

3.2.1 The preparation of cis-Pt(RDP)$_2$Cl$_2$

3.2.1.1 Synthesis

The 1,5 - cyclooctadiene (COD) in Pt(COD)Cl$_2$ is labile due to (i) the high trans - influence of the Cl group and (ii) the greater electronegativity of Cl, which contracts the Pt - 5d orbitals and synergistically weakens the Pt-COD bond. Therefore a variety of ligands readily displace COD from Pt(COD)Cl$_2$, forming a series of complexes of general formula PtL$_2$Cl$_2$. Herein we describe the displacement of COD from Pt(COD)Cl$_2$ by ruthenium-containing dendritic phosphine (RDP) to give cis-Pt(RDP)$_2$Cl$_2$.

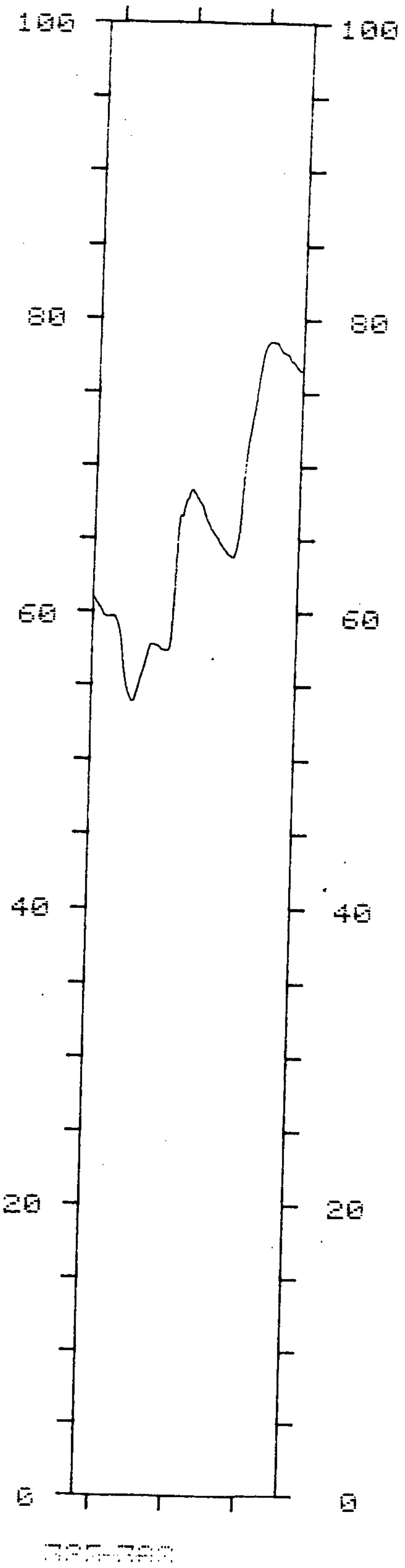
Cis-Pt(RDP)$_2$Cl$_2$ was prepared by replacement of COD from Pt(COD)Cl$_2$ by RDP ligands (produced in situ), as shown in Scheme 3.1. Two molar equivalents of RDP ligand (produced in situ) were reacted with one molar equivalent of Pt(COD)Cl$_2$ at room temperature for 3 hours. After reaction, the solvent and displaced COD were removed under reduced presure. The resulting cis-Pt(RDP)$_2$Cl$_2$ was purified on an alumina column, eluted with ethylacetate and a yellow glassy solid was obtained after precipitation from CH$_2$Cl$_2$/hexane at -15°C. The low yield (ca.29%) is due to the bulky RDP ligand complex being strongly absorbed by the alumina column. This ruthenium-containing dendritic phosphine platinum complex can be considered as a heterobimetallic dendrimer which contains platinum as core and ruthenium on the periphery. It is thermally unstable and has a decomposition temperature of 55°C.



Scheme 3.1 The synthetic scheme for cis-Pt(RDP)$_2$Cl$_2$

3.2.1.2 Characterization

The IR spectrum of cis-Pt(RDP)$_2$Cl$_2$ was recorded in a CsI pellet and shows two absorption bands at 2013, 1945 cm^{-1} corresponding to υ(CO) , which are in the same position as for the starting material, Rp3G1BR. Two Pt - Cl stretching frequency bands, as shown in Figure 3.4, were found at 316, 282 cm^{-1} in the infrared spectrum, characteristic of cis-Pt(RDP)$_2$Cl$_2$.



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PERKIN-ELMER 983

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          CsI Pellet

OPERATOR

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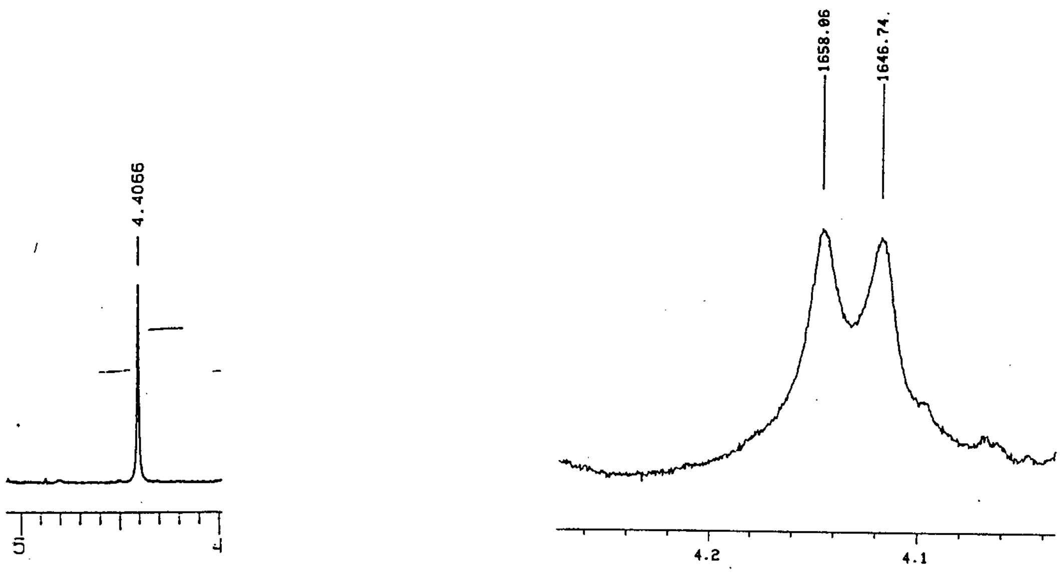
RESOLUTION           3.0
ORDINATE MODE         %T
RANGE    330.0-  260.0
ABSC. SCALE         2.00
GRATING CHANGES
  1600 600 300 CM-1

PEAK THRESHOLD   2 %T
   CM-1          %T
  316.0        54.01
  282.0        63.84
```

Figure 3.4 Infrared spectrum of cis-Pt(RDP)$_2$Cl$_2$ in the 330 - 260 cm^{-1} region

This ruthenium-containing dendritic phosphine platinum complex, $Pt(RDP)_2Cl_2$ was also characterized by ^1H , ^{13}C as well as ^{31}P NMR spectroscopy. The organoruthenium functional groups on the periphery of the RDP give four sets of resonances at positions: δ5.24 (Cp), 3.77 (CH_2O), 1.92 (CH_2), and 1.65 ($RuCH_2$)ppm. The resonances of the aromatic protons of the RDP occur in two regions: (i) δ7.41 - 6.99ppm, which can easily be assigned to phenyl protons (ii) δ6.41-6.39ppm, corresponded to aromatic protons of the dendritic wedge. Perhaps the most important information one can obtain from ^1H NMR is the resonances due to the benzyl CH_2 of the dendritic wedge. The benzyl CH_2 of RDP gives a doublet resonance at ca.4.15ppm (arising from coupling with ^{31}P nuclei), whereas the starting material, Rp3G1Br shows a singlet resonance at ca.4.40ppm, as seen in Figure 3.5.



Rp3G1Br

cis-$Pt(RDP)_2Cl_2$

Figure 3.5 ^1H NMR spectrum of RDP and Rp3G1Br in the region of 4.0 - 4.8ppm

^{13}C NMR spectroscopy was also found to be a useful tool for the confirmation of the formation of this new complex. The resonances due to benzyl CH_2 groups are clearly distinguishable from the other groups, such as CH_2Br and CH_2PPh_2. The resonance of the benzyl CH_2 of the starting material, Rp3G1Br is at ca.34ppm, as seen in Figure 3.6, however the resonance of the benzyl CH_2 of this new complex, $Pt(RDP)_2Cl_2$ is at ca.38ppm, as seen in Figure 3.7.

^{31}P NMR spectra of the complexes of the type $Pt(PPh_{3-n}R_n)_2Cl_2$, where R = alkyl and n = 1, 2, or 3, show that the ^1J (^{195}Pt - ^{31}P) coupling constant is always larger for the cis isomer than for the corresponding trans isomer.[8] Thus the ^1J (^{195}Pt - ^{31}P) coupling constant can be used to characterize the isomer. A ^{31}P NMR spectrum of $Pt(RDP)_2Cl_2$ in Figure 3.8 shows that the value of ^1J (^{195}Pt - ^{31}P) coupling constant is 3632Hz. This is similar to those observed for cis-[$Pt(PPh_2R)_2Cl_2$].[8] Thus, this ruthenium-containing dendritic phosphine platinum complex can be assigned as the cis isomer.

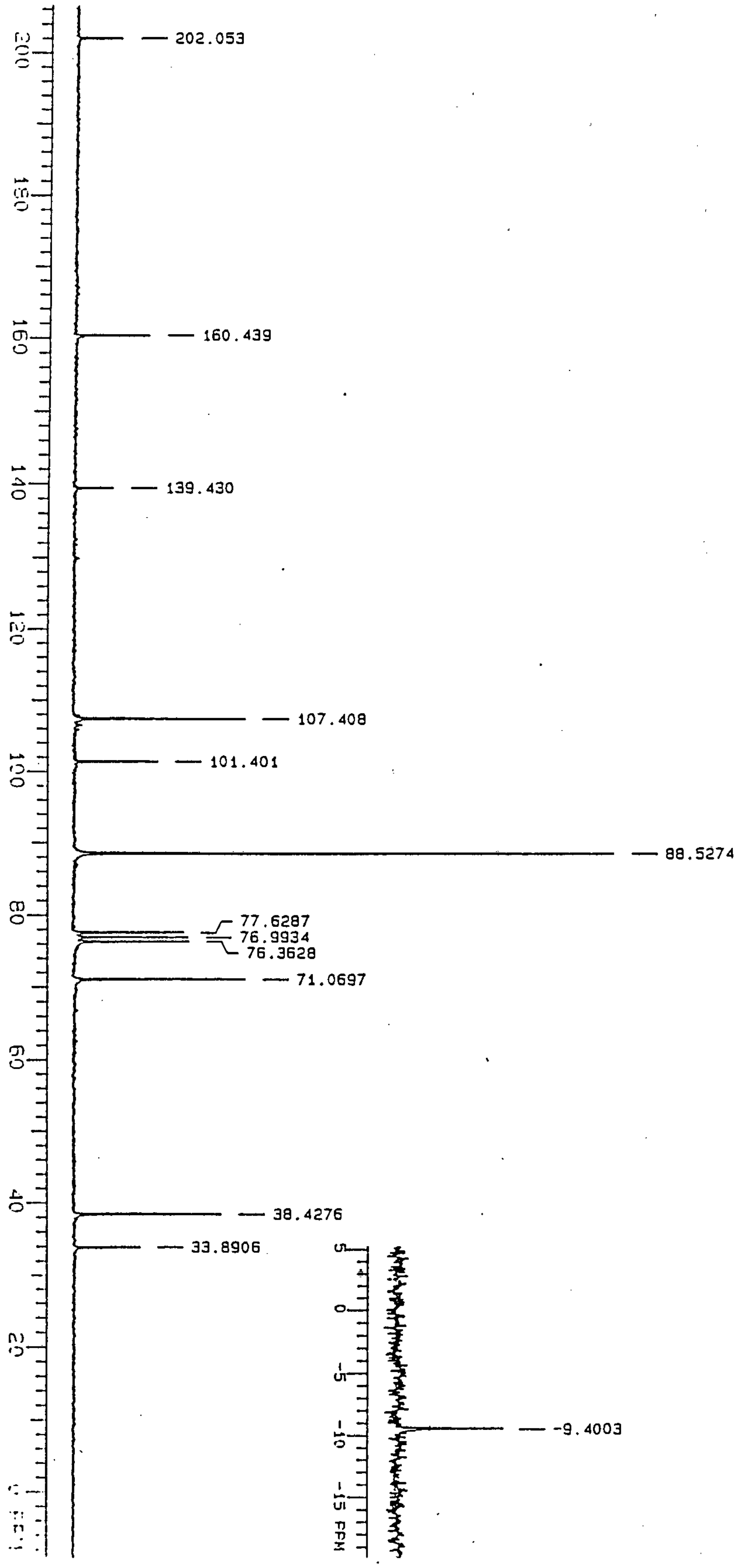


Figure 3.6 A ^{13}C NMR spectrum of starting material, Rp3G1Br

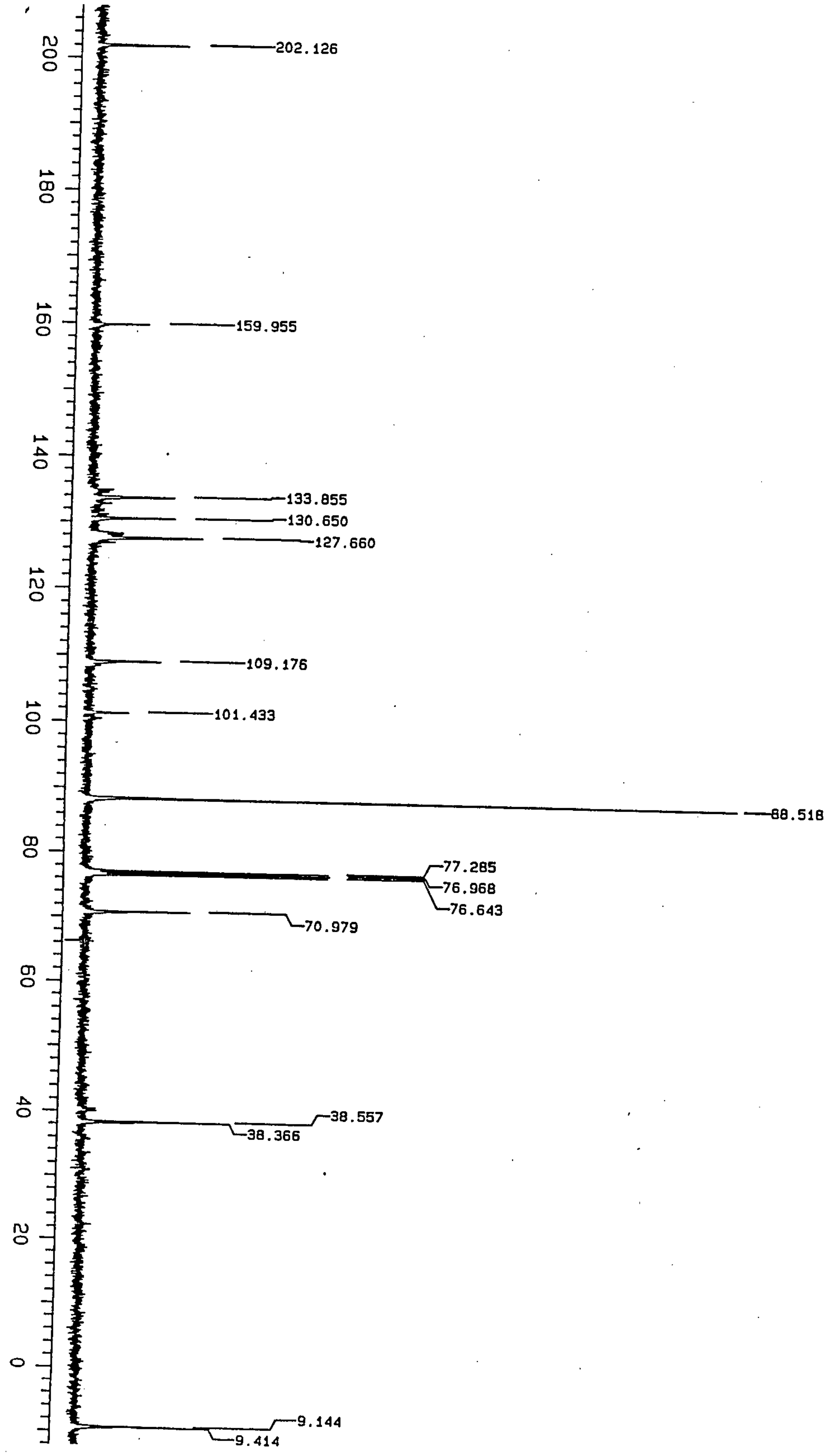


Figure 3.7 A ^{13}C NMR spectrum of organoruthenium-containing dendritic phosphine platinum complex, cis-Pt(RDP)$_2$Cl$_2$

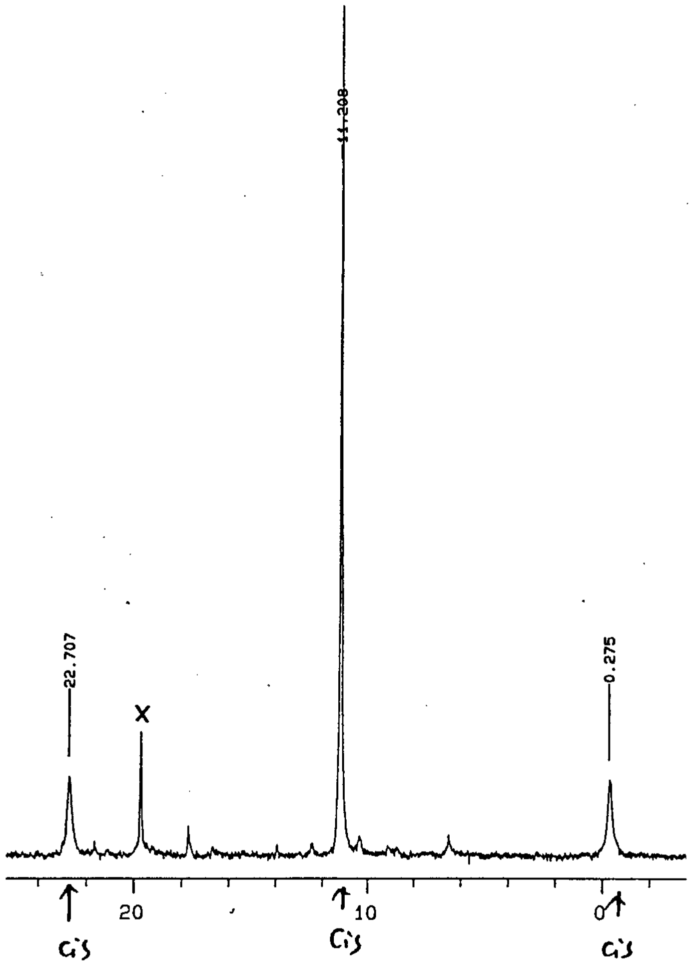


Figure 3.8 A ^{31}P NMR spectrum of organoruthenium-containing dendritic phosphine platinum complex, cis-Pt$(RDP)_2Cl_2$ (x = impurity)

3.2.2 The preparation of trans,trans,trans-$RuCl_2(CO)_2(RDP)_2$

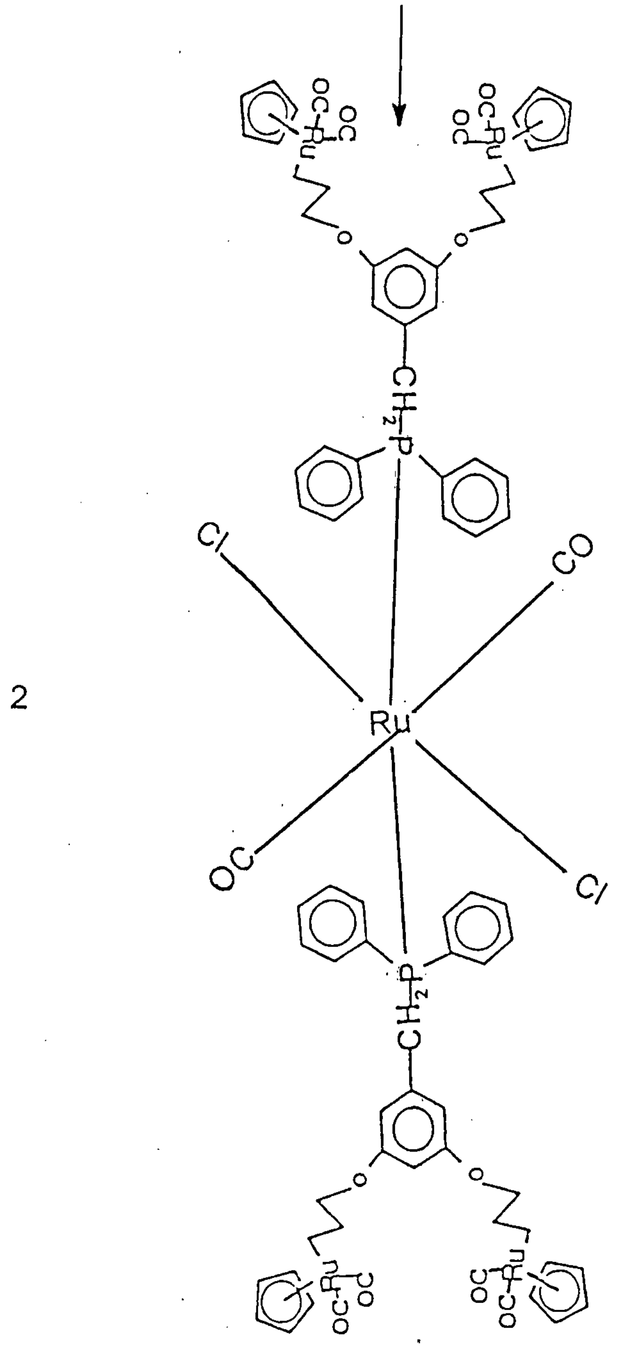
3.2.2.1 Synthesis

The complexes of the type $[RuX_2(CO)_2L_2]$, where X = Cl, Br, or I and L = PR_3 or AsR_3 were prepared by established methods.[9-12] Here we describe the synthesis of the new complex, $RuCl_2(CO)_2(RDP)_2$ of the above type. The synthetic scheme is shown in Scheme 3.2. Four molar equivalents of ruthenium-containing dendritic phosphine (RDP) ligand (produced in situ) were reacted with one molar equivalent of $[RuCl_2(CO)_3]_2$ at room temperature for 1.5 hours. After reaction, the resulting yellow glassy product, trans,trans,trans-$RuCl_2(CO)_2(RDP)_2$ was purified by chromatography.

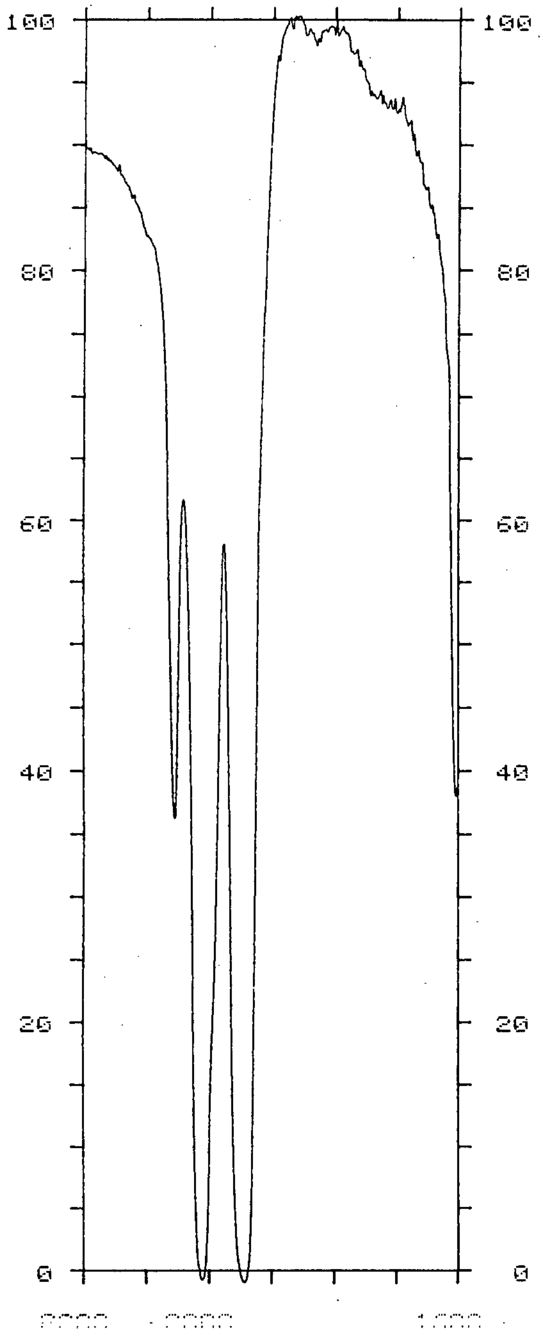
3.2.2.2 Characterization

This new dendritic phosphine ruthenium complex has ruthenium coordination geometry with trans carbonyls, trans chlorides and trans phosphines as suggested by its IR, ^{13}C NMR and ^{31}P NMR spectra. The IR spectrum of $RuCl_2(CO)_2(RDP)_2$ has three bands in the carbonyl region, as seen in Figure 3.9. Two equally intense bands at approximately 2010 and 1942 cm^{-1} are due to CO in the RDP ligand. One IR band at 2055 cm^{-1} belonging to the CO which coordinates with the central ruthenium atom, can not indicate whether $RuCl_2(CO)_2(RDP)_2$ is trans - coordinated, i.e. has trans carbonyls, since the other υ(CO) band for the central Ru could be hidden under the strong υ(CO) band of the RDP ligand. There is only one IR band in the region of 350 - 250 cm^{-1} which is due to the ruthenium - chlorine stretch. This indicates that $RuCl_2(CO)_2(RDP)_2$ has trans chlorines. The ^{13}C NMR spectrum of this complex has a single 1:2:1 triplet for the two carbonyls at approximately 192 ppm with a relatively small ^2J (P - C) coupling constant of approximately 10Hz. This demonstrates that the carbonyls are chemically equivalent and are cis to both phosphines. There is no doubt that the stereochemistry of this $RuCl_2(CO)_2(RDP)_2$ complex is trans since in addition to the IR and ^{13}C NMR evidence it has a large ^2J (P - P) coupling constant of approximately 368Hz and its colour is yellow (whereas the cis,cis,trans-isomer is white).[13]

$[RuCl_2(CO)_3]_2$ + 4 RDP



Scheme 3.2 The synthetic scheme for trans,trans,trans-$RuCl_2(CO)_2(RDP)_2$



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PERKIN-ELMER 983

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        CsI Pellet
OPERATOR

SCAN MODE            4
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RESOLUTION         3.0
ORDINATE MODE       %T
RANGE 2200.0-1600.0
GRATING CHANGES
  1600 600 300 CM-1

PEAK THRESHOLD   2 %T
  CM-1          %T
2055.0       36.19
2010.0   -    0.74
1942.0   -    0.93
1830.0       97.90
```

Figure 3.9 Infrared spectrum of trans,trans,trans-$RuCl_2(CO)_2(RDP)_2$ in the region of 2200 - 1600 cm^{-1}

3.2.3 Potential application of the ruthenium-containing dendritic phosphine platinum(Ⅱ) chloride complex in hydroformylation

Ligand-stabilized platinum (Ⅱ) - Group IVB metal halide complexes have been found to catalyze the homogeneous hydroformylation of olefins to aldehydes. With the preferred catalyst composition, bis (triphenylphosphine) platinum (Ⅱ) chloride - tin (Ⅱ) chloride, α-olefin hydroformylation proceeds under mild conditions [60 -80°C, 800 - 1500 psig H_2 / CO (1:1)], to give good yields of aldehyde (85 - 90 mol %), and high selectivity of the desired linear aldehyde [85 - 93 mole %, eg.2].[14]

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{Pt(PPh_3)_2Cl_2\ /\ SnCl_2} RCH_2CH_2CHO \qquad (2)$$

The new dendritic phosphine platinum (Ⅱ) chloride complex, cis-$Pt(RDP)_2Cl_2$ may catalyze the hydroformylation of α-olefins to aldehydes in good yields with high selectivity due to the novel dendritic phosphine ligands and the catalytically active ruthenium on the periphery. Such dendrimer-supported platinum complex catalysts should be easy to seperate from the reaction mixture. The application of dendritic phosphine complexes will be a focus of our future research.

3.3 Conclusion

A new bulky ruthenium-containing dendritic phosphine ligand, RDP can be synthesized from a first generation ruthenium-containing dendritic benzyl bromide. This versatile phosphine ligand reacts with a series of metal complexes, such as Pt(COD)Cl_2, $[RuCl_2(CO)_3]_2$ to give dendrimer-supported metal complexes which can be characterized by IR and NMR. The dendrimer-supported platinum(II) chloride complex, cis-Pt$(RDP)_2Cl_2$ may have application in the hydroformylation of α-olefins to aldehydes.

3.4 Experimental

3.4.1 Methods

Melting points were recorded on a Kofler hot stage microscope (Reichert Thermovar) and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer using CsI pellets. ^{1}H NMR , ^{13}C NMR and ^{31}P NMR spectra were recorded on a Varian Unity 400 spectrometer. All NMR spectra were recorded in $CDCl_3$ solution. Chemical shifts are given in ppm. ^{1}H and ^{13}C NMR spectra are referenced to internal tetramethylsilane (TMS), and ^{31}P NMR spectra are referenced to external 85% H_3PO_4.

3.4.2 Materials

All chemicals were obtained commercially, unless otherwise stated. Lithium diphenylphosphide ($LiPPh_2$)[15] and the first generation organoruthenium dendritic wedge, i.e. Rp3G1Br,[6,16] $Pt(COD)Cl_2$[17] and $[RuCl_2(CO)_3]_2$[18] were prepared by literature methods. Alumina (Merck, 90, active, neutral) was deactivated before use. Tetrahydrofuran (THF) was distilled over sodium wire and benzophenone. Dichloromethane (CH_2Cl_2) was distilled over anhydrous $CaCl_2$. Acetone was distilled over drierite. All the other solvents were reagent grade and used without further treatment, unless otherwise specified.

3.4.3 Preparation of ruthenium-containing dendritic phosphine metal complexes

All reactions were carried out under a nitrogen atmosphere using standard Schlenk tube techniques.

Preparation of cis-Pt(RDP)$_2$Cl$_2$

A portion of freshly made red LiPPh$_2$ (0.207mmol) in THF solution (2 ml) was transferred via a syringe to a Schlenk tube and kept at -78^{0}C (dry ice/acetone bath) for 10 min. A solution of a first generation ruthenium dendritic wedge, Rp3G1Br (0.122g, 0.166mmol) in dry THF (4 ml) was added dropwise into the above stirred LiPPh$_2$ solution at -78^{0}C. The reaction was stirred at -78^{0}C for 30 min.; the bath was then removed and the stirring of the mixture was continued for another 2 hours while it was allowed to warm up to room temperature. The resulting orange solution was added dropwise to a solution of Pt(COD)Cl$_2$ (0.031g, 0.0830mmol) in dry THF (2ml). The mixture was stirred for 3 hours at room temperature, and then the solvent was removed under reduced pressure. The residue was then dissolved in minimum quantity of CH$_2$Cl$_2$, transferred to an alumina column, and eluted with ethylacetate. A pale yellow band was collected and the solvent was removed to give a pale yellow oil. The yellow glassy solid was obtained after precipitation from CH$_2$Cl$_2$/hexane at -15^{0}C.

Yield: 0.0457g (29%); m.p.: 55-60^{0}C (decomposition)

IR (CsI pellet) υ(CO): 2013s, 1945s cm^{-1}

υ(Pt-Cl): 316, 282 cm^{-1}

^{1}H NMR δ (CDCl$_3$)ppm: 7.41-6.99 (complex m, 20H, PhH), 6.41 (broad, 4H, Ar), 6.39 (broad 2H, Ar), 5.24 (s, 20H, Cp), 4.15 (d, J = 11Hz, 4H, ArCH$_2$), 3.77 (t, J = 6Hz, 8H, CH$_2$OAr), 1.92 (m, 8H, CH$_2$), 1.65 (m, 8H, RuCH$_2$);

^{13}C NMR δ (CDCl$_3$)ppm: 202.13 (CO), 159.96, 109.18, 101.43 (Ar), 133.86-127.66 (complex m, Ph), 88.52 (Cp), 70.98 (CH$_2$OAr), 38.56 (CH$_2$), 38.37 (ArCH$_2$), -9.14 - -9.41 (RuCH$_2$);

^{31}P NMR δ ($CDCl_3$)ppm: 11.21 [^{1}J (^{195}Pt-^{31}P) = 3632Hz]

Found C 47.83%, H 4.31%, Calc. for $C_{74}H_{74}O_{12}Cl_2P_2PtRu_4$ (M = 1936) C 48.40%, H 3.85%.

Preparation of trans,trans,trans-$RuCl_2(CO)_2(RDP)_2$

A portion of freshly made red $LiPPh_2$ (0.164 mmol) in THF solution (2 ml) was transferred via a syringe to a Schlenk tube and kept at -78°C (dry ice/acetone bath) for 10 min. A solution of a first generation ruthenium dendritic wedge, Rp3G1Br (0.115g, 0.157 mmol) in dry THF (4 ml) was adder dropwise into the above stirred $LiPPh_2$ solution at -78°C. The reaction was stirred at -78°C for 30 min., the bath was then removed and the stirring of the mixture was continued for another 2 hours while it was allowed to warm up to room temperature. The resulting orange solution was added dropwise to a solution of $[RuCl_2(CO)_3]_2$ (0.0202g, 0.0395mmol) in dry THF (2ml). The mixture was stirred for 1.5 hours at room temperature, and then the solvent was removed under reduced pressure. The residue was then extracted with CH_2Cl_2. After filtration, the filtrate was concentrated and transferred to an alumina column. The polarity of the eluting solvent was gradually increased from CH_2Cl_2/hexane (7: 3) to pure CH_2Cl_2. A pale yellow band was collected and solvent was removed to give a yellow oil. The yellow glassy solid was obtained after precipitation from CH_2Cl_2/hexane at -15°C.

Yield: 0.0150g (10%); m.p.: 68-70°C (decomposition)

IR (CsI pellet) υ(CO): 2055, 2010s, 1942s cm^{-1}

υ(Ru-Cl): 342 cm^{-1}

^{1}H NMR δ ($CDCl_3$)ppm: 7.78-7.33 (complex m, 20H, PhH), 6.34 (d, J = 2Hz, 4H, Ar), 6.30 (t, J = 2Hz, 2H, Ar),

5.22 (s, 20H, Cp), 4.03 (broad, 4H, $ArCH_2$), 3.83 (t, J = 7Hz, 8H, CH_2OAr), 1.84 (m, 8H, CH_2), 1.61 (m, 8H, $RuCH_2$);

^{13}C NMR δ ($CDCl_3$)ppm: 202.11 (CO), 191.75 (t, J = 10Hz, CO),159.56, 108.85, 100.38 (Ar), 133.71-128.09 (complex m, Ph), 88.56 (Cp), 70.77 (CH_2OAr), 38.53 ($ArCH_2$), 38.36 (CH_2), -9.24 - -9.34 ($RuCH_2$);

^{31}P NMR δ ($CDCl_3$)ppm: 19.99 [^2J (P - P) = 368Hz]

Found C 49.40%, H 4.08%, Calc. for $C_{80}H_{74}O_{14}Cl_2P_2Ru_5$ (M = 1898) C 50.63%, H 3.93%.

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