ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

SYNTHESIS OF PYRROLE-IMINE SCHIFF BASE LIGANDS AND THEIR COMPLEXES WITH GROUP IVB METAL (Ti, Zr, Hf)

M.Sc. THESIS

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Thesis Advisor: Prof. Dr. Ozan Sanlı ŞENTÜRK

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

PİROL-İMİN SCHIFF BAZI LİGANDLARININ SENTEZİ VE GRUP IV METALLERİ İLE KOMPLEKSLERİ (Ti, Zr, Hf)

YÜKSEK LİSANS TEZİ

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OCAK 2021

Cahit Can ÇANAKÇI, a M.Sc. student of İTU Graduate School of Science Engineering and Technology student ID 509171228, successfully defended the thesis entitled "SYNTHESIS OF PYRROLE-IMINE SCHIFF BASE LIGANDS AND THEIR COMPLEXES WİTH GROUP IVB METAL (Ti, Zr, Hf)", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission :20 January 2021
Date of Defense :15 February 2021

To my family and friends,

FOREWORD

First of all, I would like to express my gratitude for his encouragement and support during my thesis research to my supervisor, Prof. Dr. Ozan Sanlı ŞENTÜRK.

I would like to thank to the Head of the ARCELIK A.S Central Research & Development Department Nihat BAYIZ and Materials Technologies Manager Dr. Mustafa SEZER for sponsoring myresearches. I would like to express my heartfelt appreciation to Polymer & Chemistry Team Leader Orkun KAYMAKÇI for his encouragement and support all the time.

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Also, I would like to thank to all members of my family for helping me deeply on all fronts. It would be just an imagination to do this without their faithfulness and motivation.

January 2021

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(Chemist)

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ABBREVIATIONS

ATR **:** Attenuated Total Reflectance
Comp **:** Compound
FT **:** Fourier transform
HDPE **:** High Density Polyethylene
HOMO **:** Highest occupied molecular orbital
HPLC **:** High Performance Liquid Chromatography
Hz **:** Hertz
IR **:** Infrared
J **:** Coupling constant
LDPE **:** Low Density Polyethylene
LLDPE **:** Linear Low Density Polyethylene
LUMO **:** Lowest unoccupied molecular orbital
M **:** Metal
MAO **:** Methylaluminoxane
mmol **:** Milimol (10^{-3} mol)
Mo **:** Molibdenyum
NMR **:** Nuclear Magnetic Resonance
PE **:** Polyethylene
PP **:** Polypropylene
Ppm **:** Particules per million
PS **:** Polystyrene
RT **:** Room Temperature

SYMBOLS

cm	**:** Centimeter
cm^{-1}	**:** Reciprocal Wavelength
g	**:** Gram
h	**:** Hour
min	**:** Minute
mL	**:** Milliliter
^{o}C	**:** Degree Celsius
pH	**:** Power of Hydrogen
t	**:** Time

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SYNTHESIS OF PYRROLE-IMINE SCHIFF BASE LIGANDS AND THEIR COMPLEXES WİTH GROUP IV METALS (Ti, Zr, Hf)

SUMMARY

Plastics are one of the most essential crude products and, much like our daily lives, are extraordinarily normal in wide variety of mechanical stuff. Plastic grocery bags, meal packets, shampoo, cans, plastic bins, clothings and internal – external parts of vehicles are included in the products. Along these lines, they have become key materials for present day living and legitimately sway our every day lives in endless advantageous manners.

In around the world, the all out plastics utilization will have a normal development pace of %8 in a year and to arrive at 370.5 million tons by 2018.

In Turkey, in 2020, 9.46 million tons of plastic raw materials production in were made. Output was relied on in the second quarter of 2020 to continue at the comparable pace.

Polyethylene is the most common known materials used in our day-to-day lives and reports 42% of the over all amount plastic usage worldwide thanks to its easy treatment, minimal production costs and extremely modified physical properties.

These days, many millions tons of polyethylene (PE) are being delivered by customary techniques; metallocene catalysts, Ziegler-Natta catalysts, Phillips catalysts and radicalic polymerization. However, these methods restricted item designer to analytical models and responses to trials and errrors. As a result, it took a lot of time for the design of products then it does now using molecular architecture techniques.

During the 1990s polyolefin makers had the option to utilize a way to deal with "creating and fitting" polymers by development of metallocene catalysts innovation. Thus, during the two decades, a considerable number of research activities both academic and industrial sector centered on highly active and single site catalysts, called metallocene and non-metallocene catalysts, which regulate olefinic monomer polymerization.

Group VI (Ti, Zr, Hf) metallocene and non-metallocene catalysts were the leading players in the production of a variety of polymers which improved performance. In comparision to the multi-located heterogenous Philips and Ziegler-Natta catalyst, thesecatalyst usually own a well defined homogenous active single position. Molecular catalysts thus provide advantages of chain transmission control, comonomer integration and polymer chemistry, offering access to different polyolefine substance with particular microstructures.

The motivation behind our examination is illumination of IVB group metals complexes and synthesis of new nonsymmetric ligands. Moreover, these complexes activations for polyethylene synthesis is an another important point for our study.

Generally, transition metals naturally have olefine inclusion capacity, the ratio of a metal and electronically adaptable ligands able to manage the cost of a profoundly

dynamic ethylene polymerization catalysts. Among traditional catalyst materials, ligands are the most prevalent function in polymerization catalyst. For high activity ligand oriented catalyst, the electronically flexible were needed.

Nonsymmetric ligands and their metal complexes were evaluated as olefin polymerization catalyst because their stereochemistry is very useful for production of ethylene. The name essentially dynamic ligands (FALs) were meant to electronically adaptable ligands that able to gain electrons from the planning ethylene through a metal and discharge electrons at point required to facilitate the ethylene inclusion process. In a general sense dynamic ligands commonly have even electron-giving and pulling back properties, which are foreseen to speed up olefin polymerization forms.

Central point of this postulation focus on plan and set up another arrangement of pyrrole-imine non-symmetric ligands, named 1-2. They were then used to get ready novel Group IVB metal [M = Ti; (a), Zr; (b), Hf; (c)] comolexes, named 1a-1c, 2a-2c, The complexes thus can be utilized as olefin polymerization catalyst.

The molecular structuree of these new nonsymmetric ligands (1-2) were examined by utilizing the accompanying spectroscopic techniques: FT-IR, ^{1}H-NMR, ^{13}C-NMR.

The IVB metal [M = Ti; (a), Zr; (b), Hf; (c)] buildings, 1a-1c, 2a-2c, 3a-3c were integrated with new nonsymmetric ligands which are deprotonated, 1-2 and group IVB metal salts MCl_4 [M = Ti; (a), Zr; (b), Hf; (c)]. Their structures were researched by utilizing the FT-IR, ^{1}H-NMR, ^{13}C-NMR spectroscopic strategies.

PİROL-İMİN SCHIFF BAZI LİGANDLARININ SENTEZİ VE GRUP IV METALLERİ İLE KOMPLEKSLERİ (Ti, Zr, Hf)

ÖZET

Plastikler sentetik ve yarı sentetik organic polimerler olarak tanımlanmaktadır. Bir başka deyişle, farklı elementler içerse de, plastikler her zaman karbon ve hidrojen içermektedirler. Plastikler hemen hemen bir çok polimerden yapılıyor olsa da, endüstriyel plastikler petrokimyasallardan yapılmaktadırlar. Termoplastikler ve termosetler iki tip farklı plastic türünü temsil etmektedir ve "plastic" kelimesi kırılmadan deforme olma kelimesinden gelmektedir.

Poliolefin malzemelerde bu plastik sınıfı malzemeler açısından en çok üretilen ve en çok kullanılan malzeme sınıfı içerisindedir. Bu kategoriye; polietilen(PE) , polipropilen (PP) , a-olefinler ve etilen- propilen-dien elostomerler dahil olmaktadır.

Plastik sektörü oldukça hızlı büyüyen bir sektördür ve 2018 yılının raporlarına bakıldığında 359.000.000 milyon tona ulaşmış bir üretim kapasitesi mevcuttur.Bu rakamın daha da artacağı öngörülmektedir.

Polietilen (PE) fiyat – performans kriterleri açısından incelendiğinde günümüzde en çok tercih edilen polimerlerin başında gelmektedir.Dünyada plastik sektörünün %40'ını , Türkiye'de ise %45'e yakınını bu polietilen oluşturmaktadır.

Polietilen sentezinde hali hazırda uzun bir süredir klasik metodlar kullanılmaktadır.Bunlar içinde , Philips sistemi, radikalik polimerizasyon , Ziegler Natta sistemi ve metalosen katalizörler ile gerçekleşmektedir. Genel olarak bu katalizörlerin verimi düşük olması nedeniyle pazar payı azalmaktadır.Bu sebeplede yüksek verimli yeni nesil olefin katalizörlere ihtiyaç duyulmaktadır.

Ziegler-Natta katalizörlerine göre moleküler katalizörler homojen bir yapıya sahip oldukları için , Ziegler-Natta çoklu merkeze sahip olsa dahi poliolefin sentezlerinde daha kontrollü ve daha spesifik sentez reaksiyoları yapabilmektedirler.

Tek merkezli metalosen ve non-metalosen yapıların sentezi ile endüstriyel ve akademik çalışmalar bu yönde hız kazandı.Bir olefin polimerizasyon katalizöründe metal , ligandlar , polimer zinciri, koordine olmuş olefin ve aktivatör bulunur.

Non-metalosen yapılar dört ana kısımdan meydana gelir; alkil grup, geçiş metali , yardımcı katalizör ve ligand. Bu başlık ta ki şüphesiz en önemli konu ligand tasarımıdır.Bu nedenle orijinal non-metalosenleri elde etmek için "liganda özgü tasarım" gerçekleştirilmelidir. Olefin polimerizasyonunda bir katalizörün yüksek aktivite göstermesi için bulundurması gereken özellikler ;

- Kompleks yapma kapasitesinin yüksek olması.
- Ligandın bağlanabileceği cis konumlarının metal üzerinde bulunması.
- Kompleks tek çekirdekli olmalıdır.

- Katalizörün merkez metal atomu yüksek oksidasyon içermelidir.

Elektronikçe esnek bir ligand ve bir geçiş metalinin reaksiyona girmesi ile oluşan kompleks bileşik , verimli bir polimerizasyon reaksiyonu yapabilir. Elektronikçe esnek ligandlar elektron verme-çekme özelliğine sahip olması anlamına gelmektedir ve ayrıca HUMO – LUMO enerji seviyeleri arasında küçük bir farka sahip olmasıdır. Polimerizasyon sırasında ligandların aktarılan elektronları kendi üzerinde taşıma kabiliyetine sahip olmalıdır, bu yüzden elektronikçe esnek ligandlar seçilir.

Bu sebeple bu çalışmada aktif katalizörlerin geliştirilmesine yönelik çalışma da liganda dayalı katalizör tasarımına yönelinildi.

Çalışmalar oksijensiz ve susuz atmosfer altında ve glove box içerisinde ve Schlenk teknikleri kullanılarak gerçekleştirildi.

Araştırma kapsamında pirol-imin ligandları ile 1-2 de gösterilmiş olan ligand tasarımları sentezlendi ve pirol-imin ürünleri , FT-IR , ^{13}C-NMR , ^{1}H-NMR spektroskopik yöntemleri kullanarak tayin edildi.

Aynı zamanda 1 ve 2 ligandlarını molekül yapıları tek kristal X ışını kırınımı metoduyla belirlendi.

Sodyum hidrid ile protonları koparılmış ligandların 1-2 Titanium, Zirconium ve Hafnium geçiş metal tuzları ile arasında ki tepkime ile kompleksler 1a-1c ve 2a-2c, 3a-3c reaksiyonu gerçekleştirildi. Sentezlenen yeni komplekslerin molekül yapıları FT-IR , ^{13}C-NMR , ^{1}H-NMR spektroskopik metodlarıyla belirlendi.

1. INTRODUCTION

1.1 Polyolefins

Polyolefins are polymers, such as ethylene, propylene or styrene, made using simple alkanes. They are formulated polymers that are most widely used. They talk of about half of all ware polymers and 90 percent of the worldwide supply of polymers by weight. With, different properties and different uses, there are several grades of polyolefins are available [1].

Polyolefinic materials are immense molecules described by polyethylene (PEs), polypropylene (PPs), ethylene/alphaolefin), yet they are often generated and eaten in colossal quantities.Both solid polymers have their estimated annual worldwide grow rate %8.2 plastic production and usage in 1961 were between 8 million and 195 million tons in first quarter of 2006, while 542 miilion tons in 2021, which is a forecast at more modest 7 percent each year [2, 3].

870 thousand heaps of production of plastic raw materials were carried out in Turkey in 2011. The raw fabric produced form plastics is shown in Figure 1.1. Polyolefines are manufactured by PETKİM (Petkim Petrochemical Inc.) , that's %79 of Turkey's total consumption [2].

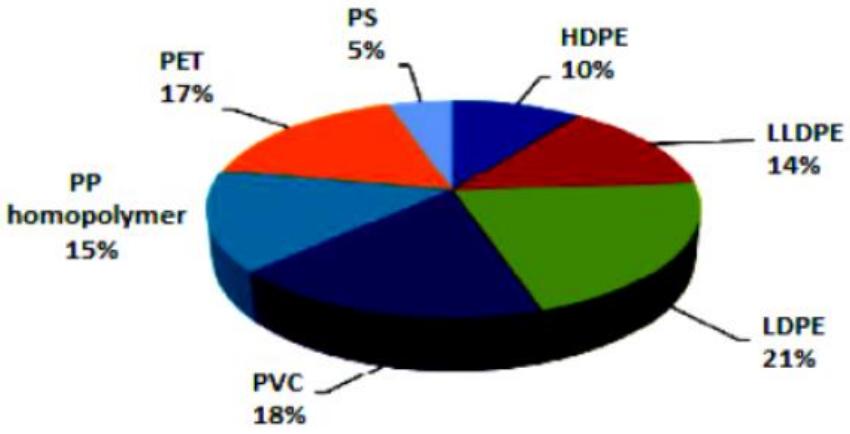


Figure 1.1 : Raw material fabrication in Turkey.

495.000 tons of plastic materials were exported in third quarter of 2011, 5.3 million tons were bought. This means that Turkey is producing less plastic metarial than its consumption[4].

Polyolefins have an unbelievable array of properties. Ultra-inflexible thermoset polyolefins are stiffer than steel with better elastomers. In addition, these products are functional and, in addition, have high latency and recyclability of the substance[1].

Usage areas include plastic grocery bags, grocery packages, cleaner bottles, holders, storage boxes, games, dispensable diapers, tennis shoes, resistant slug vests, and car indoor portions (e.g. instrument screens, running glass channels, entrance trims, fuel tanks, guards)[1]. In this way , they have been important instruments for today's lives and have legitimately shaped our everyday lives in incalculably beneficial ways.

There are hardly any composite polyolefin parts; polyethylene, polypropylene and a few polyethylene copolymers with an alpha-olefin. The main reason for this inconsistency is the molecular regulation by the cutting edge change-based metal catalysts of the polymerization process. By regulating the molecular weight, molecular weight distrubution , and tacticity, transition metal catalyst make it feasible to deliver "customized polymers" with thoroughly characterized polymers [5].

Based on early transition metals, non-metallocene and metallocene catalysts provide an important method of polyolefin production.Since the performance of the metallocene catalysts, big attempt was made to use new generation non-metallocene catalyst [6].

Although up to this stage an immense amount of classes of superior single-site impetuses have been established, developments in some parts of reactant execution (e.g. temperature stabilization, chain motion , distrubition control of comonomer arrangement, precise polymer property control) are still necessary.

For the metallocene polyolefins showcase, early figures from a variety of outside sources expect higher growth. In comparison, progress has not yet completely developed and fresh item contributions are continuing at a fast pace and pushing manufacturers are yet genuinely efficient. An ongoing evaluation by ChemSystems shows a powerful rise (Figure 1.2)[7].

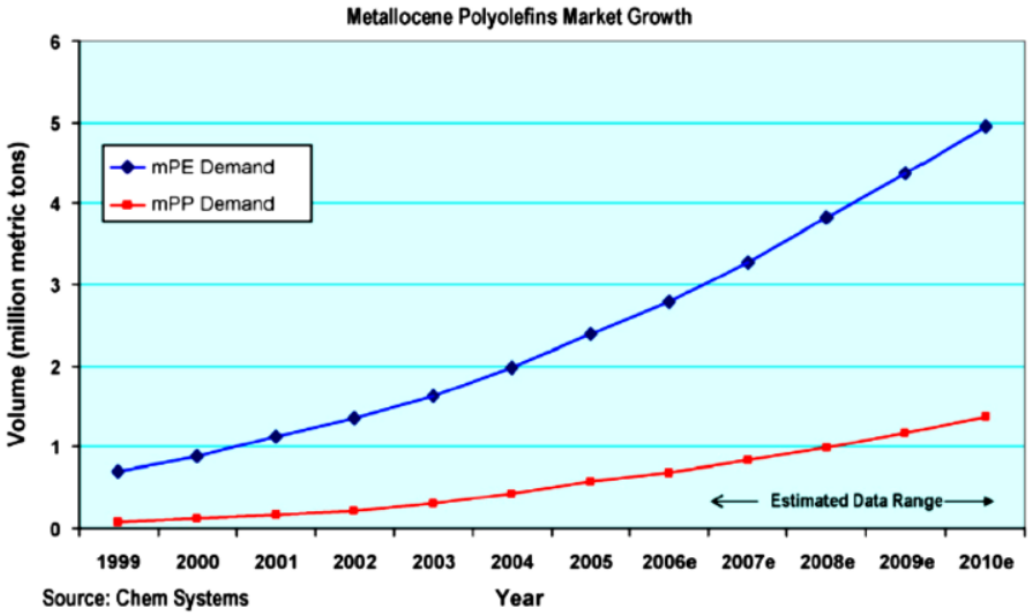


Figure 1.2 : Demand rise for polyolfines dependent on metallocene.

1.1.1 Polyethylene

Polyethylene has the shortest basic structure of any polymers, is the highest plastic tonnage and it is very common polymer than other types. The key appeal of polyetylenes are its excellent electrical features, chemical resistance, good workability, strength and durability in different types of grades and low price too [8]. Development desires are around 5.5% every year, coming to more than 84 million metric tons in 2011 [8]. Along these lines worldwide polyethylene industry experienced solid development late years and is required to keep progressing as it comes to around $138.1 billion of every 2016 [9]. Polyethylene are synthezied different ways by Ziegler, Philips and metallocenes process. Moreover, Low Density Polyethylene (LDPE) which is a polymer , produced by high pressure and high temperature via free radical polymerization[13].

Metallocene cotaning polyethylene synthesis is very limited in the sector. Analysts saw that polyethylene based plastics become widespread among other type of plastics and also in recent years, these polyethylenes based plastic have been produced by metallocene process. Polyethylenes which is produced by metallocene process is increasing day by day in the market (Figure 1.3) [7]. Researchs show that polyethylene production will increase dramatically next fiveyear. Asia will be relied upon to drive the polyethylene business because of minimal effort work, downstream preparing limit increases, and government-bolstered sponsorship bundles [9].

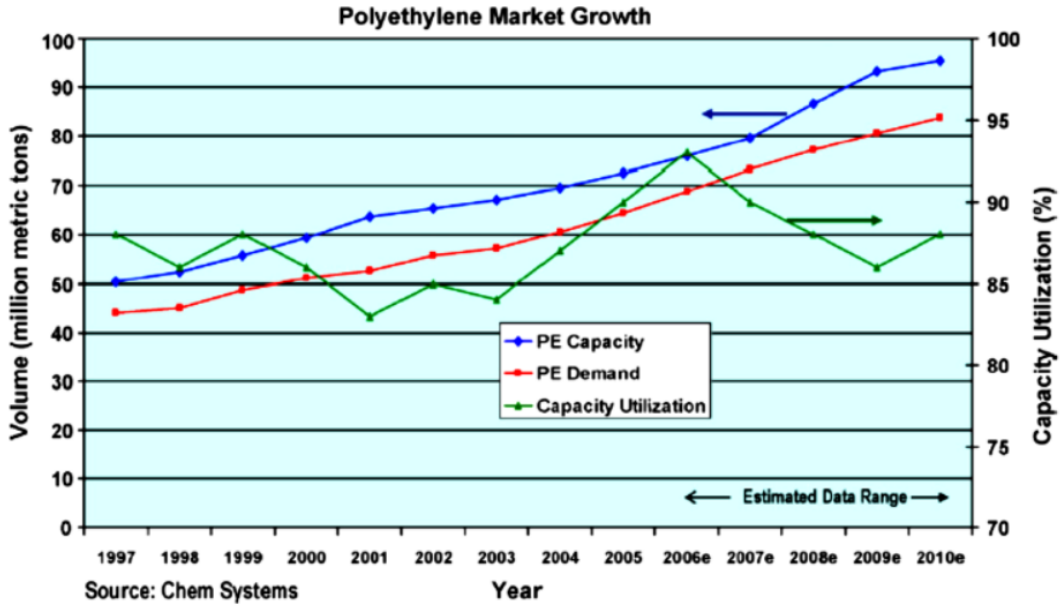


Figure 1.3 : Demand rise of PE.

1.2 Polymerization of Olefines With Catalysts Systems

Although Ziegler-Natta system is very common for production polyethylene, there are another ways to synthesize polyethylene, these are Phillips, Ziegler-Natta, metallocene and non-metallocene processes [14].

1.2.1 Phillips processes

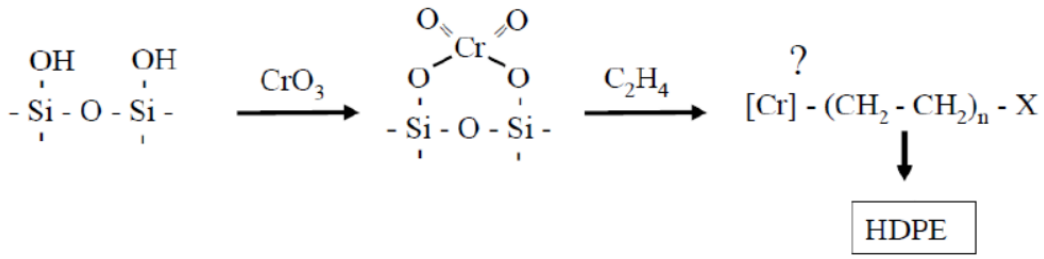


Figure 1.4 : Philips catalyst – chromium.

The Phillip process, reaction atmosphere is 140-160^{0}C and 1.4-3MPa pressure applied to dissolved ethylene in a hydrocarbon solvent. In polymerization, metal oxide is used as supporter and the solvent is very crucial for heat transfer medium. Catalyts package contains %5 chromium oxide and %95 silice by weight and for their activation 220^{0}C is very crucial. In the end of the reaction, the mixture transferred into a separator which is used for gas-liquid and then polymer is separated from the solvent with purification techniques [14].

1.2.2 Ziegler processes

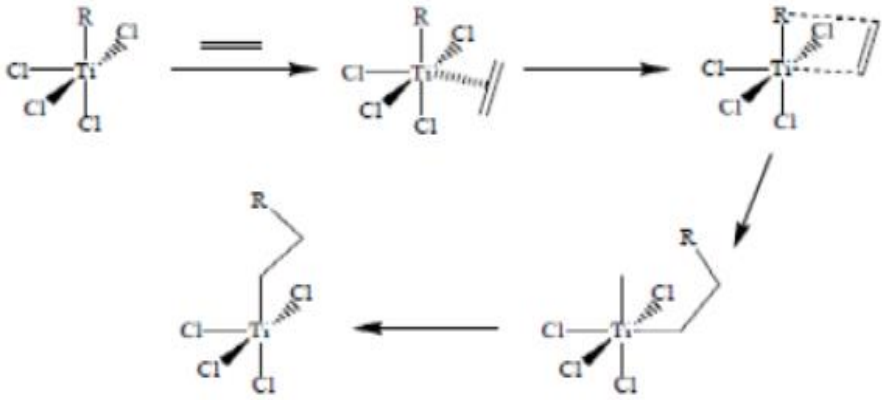


Figure 1.5 : Mechanism of monometallic ziegler-natta polymerization.

As the name of the processes, this polymerization reaction technique was found by Ziegler-Natta with their huge contributions. In this processes, titanium tetrachloride and aluminum triethyl are used for catalyst preparation and ethylene gas valve is opened and the gas is loaded slowly to the reactor which contains a solvents system for ethylene. The Polymerization is performed about 80^0C. Moreover it is important that absence of oxygen and humidity can decrease effectiveness of catalyst system [14].

1.2.3 Metallocene processes

D. Breslow (USA) proposed the idea of the metallocene which is very similar to Ziegler-Natta catalyst system which is the first metallocene catalyst system for olefine polymerization. Early researches showed that metallocene catalyst system has lower activity [15]. Kaminsky and Sinn developed a metallocene catalyst system which is higher activity than its competitors [14]. There are many dipehynl structure that can be used for preparation of Kaminsky-Sinn system.

In pentadienyl Cp2MX2; Titanium, Hafnium and Zirconium are used as M which is metal supported and X is alkyl halides. The cyclopentadienyl gatherings can convey different alkyl substituents. Bis-metallocene structure can be modified with indenyls, hydroindenyl gatherings, C9H11, or fluorenyls, C13H9 [14].

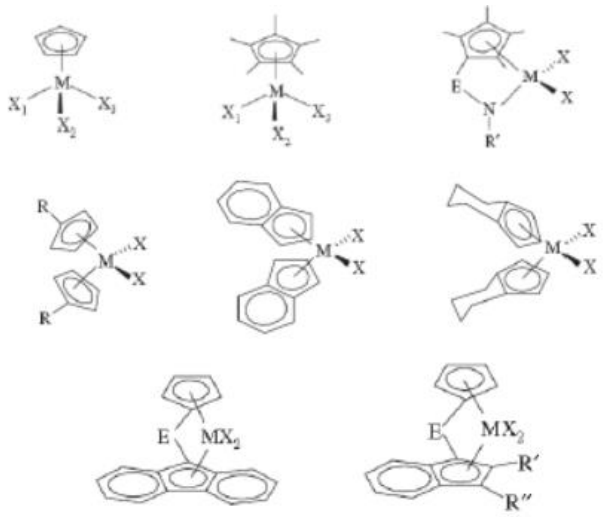
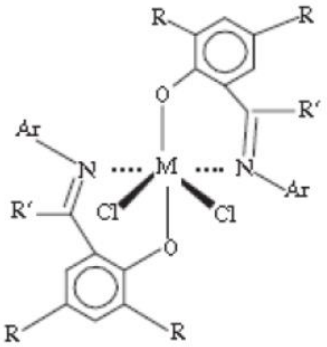


Figure 1.6 : Complexes of various metallocene catalysts.

The reason of zirconium complexes are very popular in metallocene complexes, during the studies of metallocene complexes zirconium ones are shown the hight reactivity rate. On the other hand, reaction solution is an another important parameter for synthesis enviroment. For instance, when the reaction occurs in toluene solvent system, reaction is completed with high yield and high activity. These days, metallocene catalyst systems are builded with two ways ; the first one contains one cyclopentadienyl structure , the second one contains two cyclopentadienyl ring which are linked to Group VIB elements. The two kinds of metallocene complexes were the subjects of a colossal volume of research, both in the scholarly world and in industry. These catalysts and their ensuing alterations directly contend with Ziegler–Natta procesess for some areas [15].

It is also well-known that metallocene catalysts have drawbacks in terms of usage of activators which are flourine based borons and MAO's. These activators are important for polmerization in order to get high yield. However , the activators are expensive and in the end of the polymerization reaction , they remained in the product as impurity. For this reason, it is very crucial that cost and performance balance should direct to metallocene catalyst studies [5].

1.2.4 Non-metallocene processess



M = Ti, Zr
Ar = Ph, C_6F_5
R = Me, *t*-Bu, halogen atoms

Figure 1.7 : Example of a non-metallocene catalyst forms.

In 1995, non-metallocene catalysts have gain importance in the catalysts studies, the advantage of non-metallocene catalyst was that they can use with polar comonomers and they did not need more energy in the process. Espicially, they offered lower energy synthesis route for ethylene-viniyl acetate copolymer [15]. Nowadays, homogenous catalyst system draws attention in terms of olefin reactions. The reason is that usage of non-metallocene catalyst offers to produce narrow molecular weight distribution polymer which is very crucial for both reactivity and technical properties of polymers. Morever, this system allows to discover new polymers in terms of physical properties and topologies of polymers and polymer reactions. Last ten year, catalyst industry and academia focused on non-metallocene catalyst area and number of articles are inceasing day-to-day [14].

1.3 Single-Site Catalysts

Single site molecular catalyst can be examined in two categories , which are heterogenous and homogenous and basically single site catalyts have one metal center and also this center metal should be active in terms of reactivity.

The estimation of the propagation rate constants in a polymerization reaction of a specific alkene, just as the rate constants of all chain transfer reactions, is the equivalent for all the centers. These kinetic highlights lead to a specific kind of the molecular weight distribution of any polymer produced with uniform active centers.

The chemistry of the considerable number of centers sort is equivalent. The attributes prompts an extremely limited stereoregularity distribution of alkene homopolymers [2].

Although Ziegler-Natta catalyst which is multi-sited heterogenous catalyst can not be compare its rivals espicially in terms of cost advantage. However molecular catalyst that contains group IVB metals have better reaction activity and output polymer properties [17]. For this reason , single site catalysts have advantageous in order to synthesize new and special polymers such as high and low density , tacticity , molecular weight. [16].

On the other hand,a single site catalyst which is called as post-metallocene catalyst (Figure 1.3) is quite popular in recent years because they have a ability to produce ultra high density polymers and also synthesis of copolymers that contain homopolymer can be useful , it can not be possible to produce with metallocene catalyts of group IVB.. Moreover , non-metallocene catalysts have the advantage of producing more accurate polymers and in polymerization steps[17]. There is no doubt that development of non-metallocene catalysts will be necessary for the future of catalyst chemistry and polymer industry in order to produce more efficient and active polymers.[18].

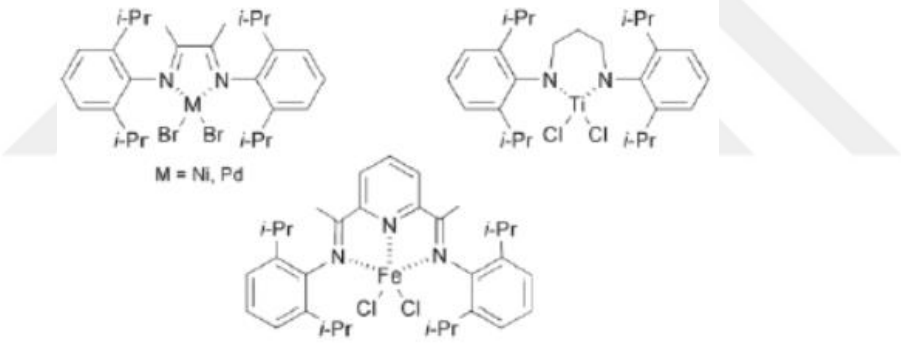


Figure 1.8 : Examples of single site catalysts which are non-metallocene.

1.4 Insertion or Coordination Polymerization

In coordination polymerization, metal-carbon bond has huge importance for insertion to olefin and metal-carbon or metal alkyl complexes can be prepared for this purpose. The disadvantageous of working with early transition metals that they are very sensitive to air moisture, for this reason co-catalst systems which are methylalumoxane(MAO) are used to alkylate the complex. In coordination polymerization, catalyst solubility is crucial because the product should separate very easily from the catalyst system. Rule of fourteen electron is (Figure 1.9), taking into account in the polymerization.

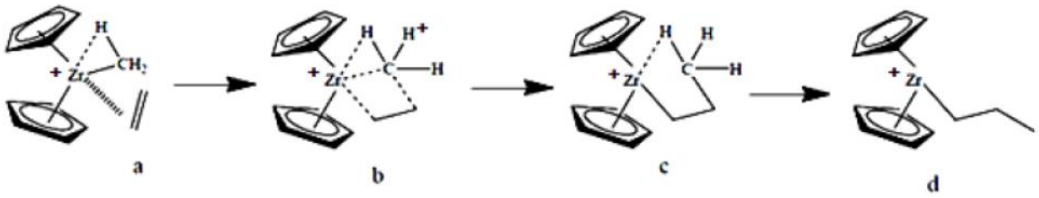


Figure 1.9 : Insertion or coordination of monomer of ethylene into a metal.

The important point in the production of polymer, the activation of both chain and metal is an initiation step for attaching double bond of monomer to metal complex and in the end of the bond cleavage, the cycle starts again and this also an indicator activity and reaction capacity for catalyst system [19].

1.5 Activation of Catalysts

In the polymerization step, it is not possible to use complexes by itself. The reason behind that especially group IVB metal contains complexes are quite sensitive to air moisture. Therefore, it is not practical to use in mass production, for this reason MAO(methylaluminoxane) became more popular and useful co-catalyst in long period of time [56]. Polymerization of olefin with metallocene and commercial aluminum alkyls is not sufficient in terms of activity but with usage of MAO the activity is increasing dramatically[34].

Chemical spectroscopic techniques supported to be found MAO that strong acids poison them [34].

Still it is unkown the mixing ratios of MAO and catalysts in order to determine best performance activity to produce polymers. The reason is that MAO is very complex oxygen and aluminum valance electron behavior [20].

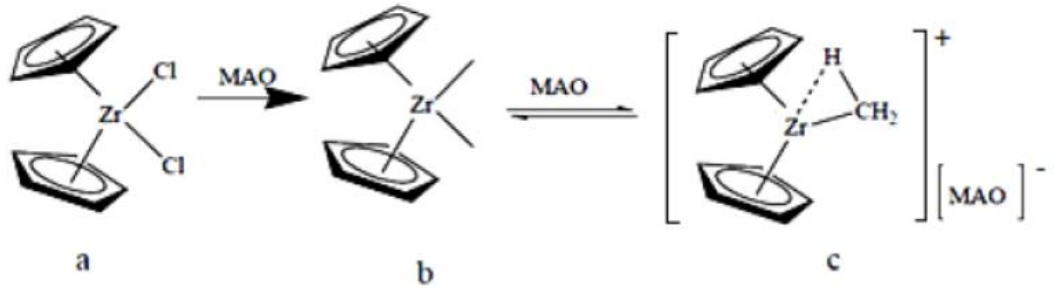


Figure 1.10 : Activation of a precatalyst metallocene by MAO.

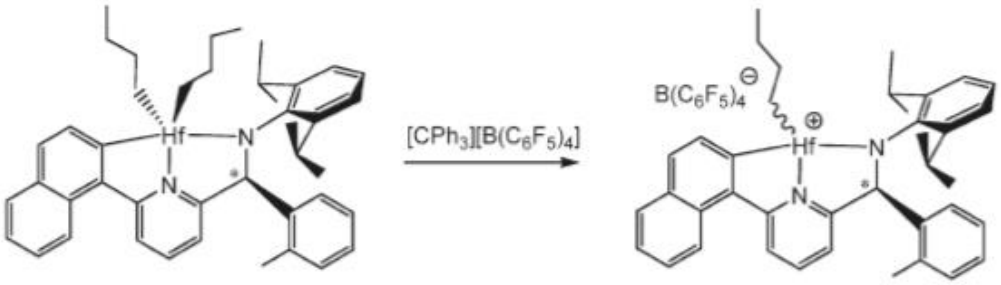


Figure 1.11 : Activation by borate cocatalyst of a Non-Metallocene precatalyst.

1.6 Termination of Polymerization

Polymer termination route determines all specific polymer properties such as polymer chain length , molecular weight and density of polymers. The termination route with MAO, which is a co-catalyst, take place with in three principle. The first one is **A**: insertion of monomer to catalyst , second one **B** : π electrons of monomer bonded to aliminum and third one **C** : cleavage occurs between MAO and polymer. In the route A, the termination is not relevant with amount of monomer but in route B, the termination is relevant with monomer amount in enviroment.In the route C, termination occurs when aliminum amount is not sufficient [21,22].

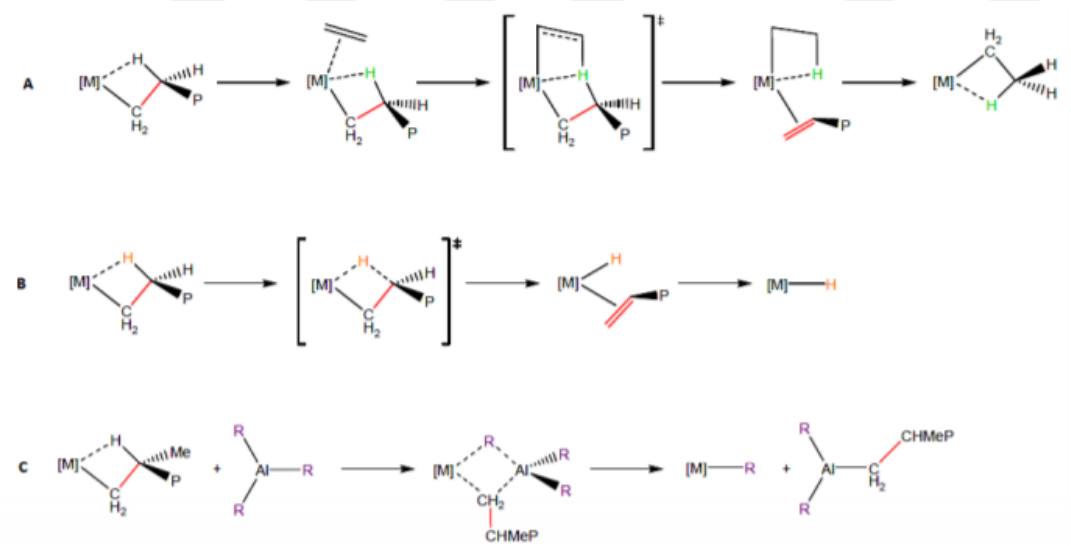


Figure 1.12 : The most important termination routes in the polymerization of etyhlene.

2. SCHIFF BASES

First time , Schiff base was synthesized by Hugo Schiff with the reaction of primary amine and carbonyl. The structure of Schiff bases are indicated with RR′C=NR″ where R can be alkyl , cyclic alkyl or aryl and also there are hundreds of group is possible to attach to the schiff base and these groups determine electronically flexibility of schiff base ligands. Schiff bases attache to metal ion with their free electron pair in azomethine nitrogen.Schiff Bases research field is a huge coordination chemistry field and covered by all chemistry departments.Moreover , They have wide usage area in painting, chemistry , biology and agricultura chemistry.

2.1 Synthesis of Schiff Bases

Acid catalyzed schiff bases synthesis is well-known procedure to obtain schiff base ligands. In this procedure , weak acids such as para-toluenesulphric acid are used in order to catalyze the reaction. In the reaction mechanism , non pair electrons of amine attacked to carbonyl carbon of aldehyde or ketone and in the end of the reaction imine formation and water occurs. The important point is in the reaction comes out differences between aldehyde and ketone steric hinderance and also carbonly carbon electropositivity. Ketone structres have more steric hinderance than aldehyde ones. Therefore , the reaction yield can decrease ketone-amine imine reaction even acid catalyst system is used. Microwave technique can be useful in order to synthesize difficult imine formation espicially ketone based systems[23].

In the Schiff base reaction, water occurs and water can decompose Schiff base ligand reversly, for this reason drying of the system is very crucial. Generally, anhydrous sulphate salts and molecular sieves can be used as dryer. Also, calcium halide is very common dryer. However , anhydrous sulphate salts can react with initial materials , thus molecular sieve is very safe method to use as a dryer in Schiff base reactions [23].

2.2 Schiff Base Complexes of Transition Metals

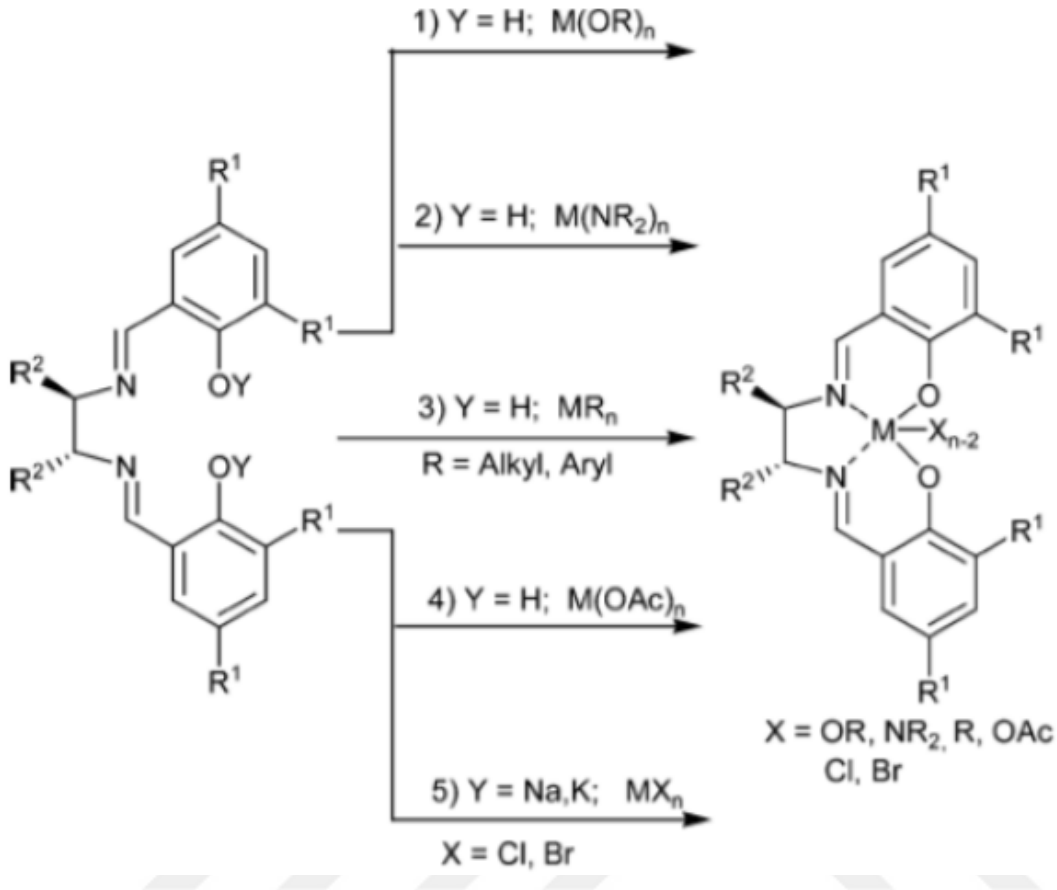


Figure 2.1 : Synthesis of salen form Schiff base complexes.

Schiff bases are not only synthesize with donor pyrrole groups but also they can synthesize with donor furane group. With this advantage , schiff bases can show different properties by itself and be reacted with metal complexes. Moreover , the difference between schiff base ligand structure determine catalytic performance of complexes when synthesis with olefines to produce polymers. Therefore , each of initial substance are important for in total output. On ther other hand , chirality of schiss base ligands presents wide of application area [23, 24].

In the literature, there are very common three routes in sytnthesis of schiff base ligands complexes [23].

Method 1 this method contain metal alkoxides, which are Titanium and Zirconium metals, are very sensitive to air moisture because in the presence of moisture in reaction conditions , metal alkooxide can decompose and the reaction fail. Therefore , it is important that the reaction should be carried out presence of nitrogen atmosphere [23].

Method 2 Metal complexes occur when Schiff base proton deprotonated by using of halides and then non-pair electron of nitrogen penetrate to d orbitals of metal. Moisture and oxygen should not be in reaction environment [23].

Method 3 In this way, Schiff base ligands reacts with IIIA group metals alkyl, which are Ga, Al and In [23].

2.3 Non-Metallocene Catalysts

2.3.1 Phenoxy-imine-based catalysts

Phenoxy-imine which used sulfonylhydrazones reaction was completed in the content of Phd studies and zirconium- hafnium metals are used as a metal ion [35]. Phenoxy-imine reactions were shown in Figure 2.2 and Figure 2.3.

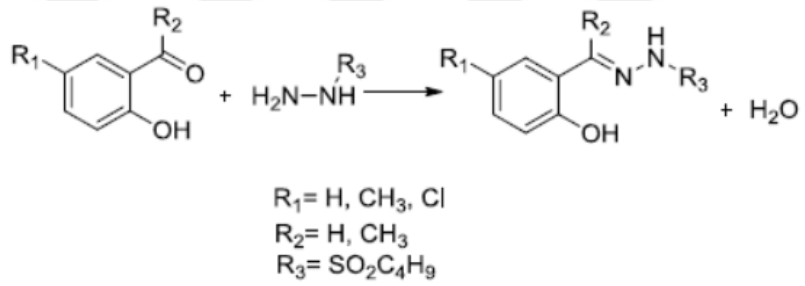


Figure 2.2 : Synthesis of Phnoxy-Imine containing Schiff bases.

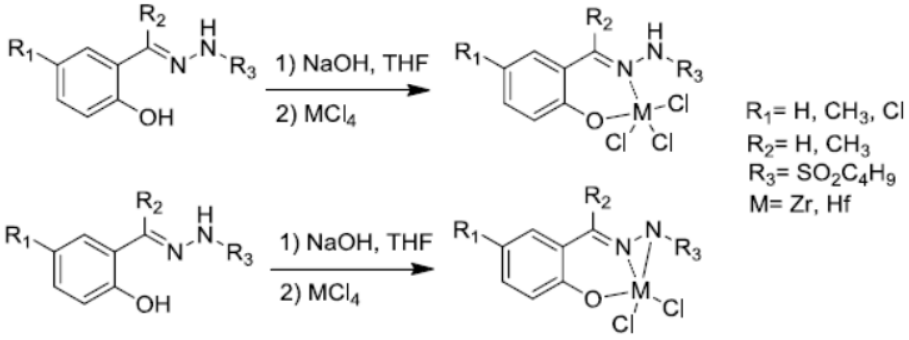


Figure 2.3 : Synthesis of phenoxy-imine based non-metallocene catalyst.

2.3.2 Pyrrole-imine catalysts

Pyrrole-imine reaction was completed in the content of Phd studies and zirconium-hafnium metals are used as a metal ion for another Phd research [36]. Synthesis of these ligands and their complexes were shown in Figure 2.4 and Figure 2.5. [36].

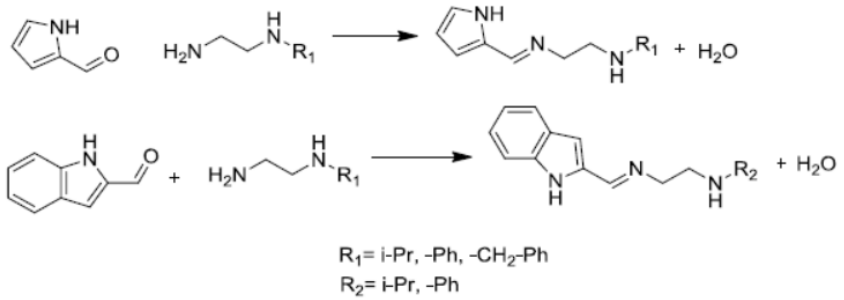


Figure 2.4 : Synthesis of pyrrole-imine Schiff bases.

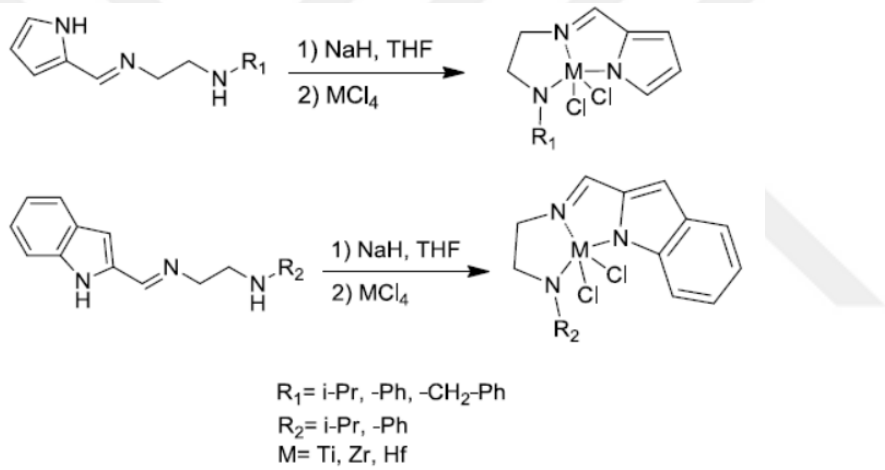


Figure 2.5 : Synthesis of pyrrole-imine non-metallocene catalysts.

Output products were indicated in Figure 2.6 [36].

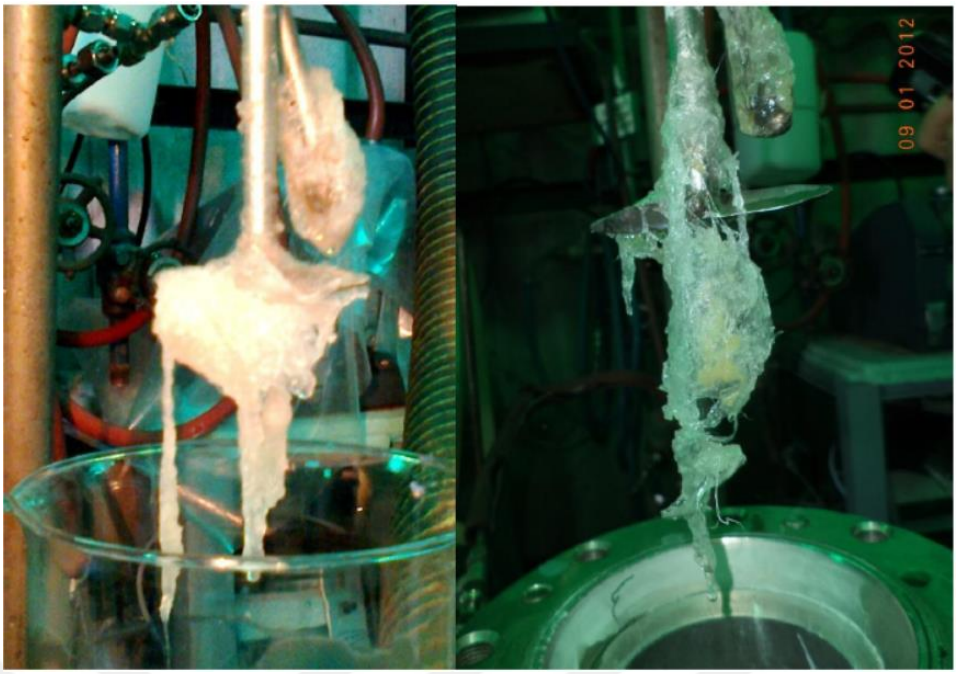


Figure 2.6 : Polyetylene products.

3. EXPERIMENTAL PART

3.1 General Information

Both manipulations for titanium, zirconium, hafnium complexes were conducted using inert (Nitrogen) which is O_2 level below 10 ppm and moisture below 2.5 ppm atmosphere and Schlenk and Innovative Glowbox equipment were used in order to obtain good results. In order to remove trace quantity water, HPLC grade solvents which purified before reactions by Innovative Solvent Purification System contains special catalyst systems.

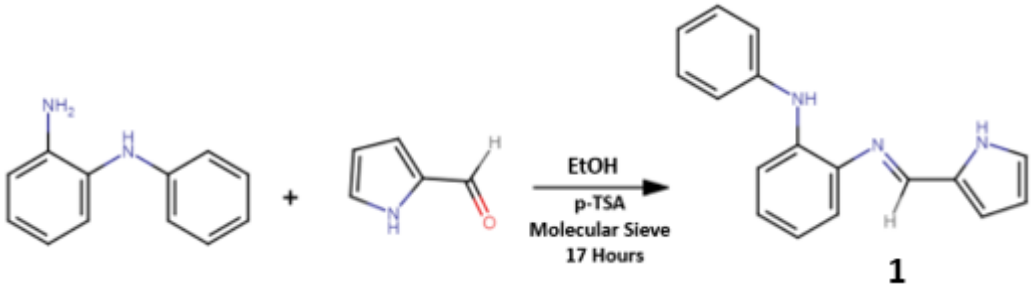
On a Bruker D8 Venture Mo Kα radiated at 100 K, crystallographic tests were carried out with graphite. Through direct use of Fourier techniques,processes and extended,both pathways have been solved and the non-hydrogen atoms became anisotropically.

In FTIR analysis, the wavelengths in the infrared region are absorbed by compunds and the compound groups are thus calculated. Hydrogen atoms were used but were not distilled. All analyses were carried out using crystallographic software packages, with the exception of refining, which was carried out using SHELXL-97

Spectra ^{1}H-NMR, ^{13}C-NMR have been recorded with tetramethylsilane as internal reference on the Agilent VNMRS 500MHz spectrometer. FT-IR Spectra are acquired from substance in a Bruker Alpha ATR inside glow box.

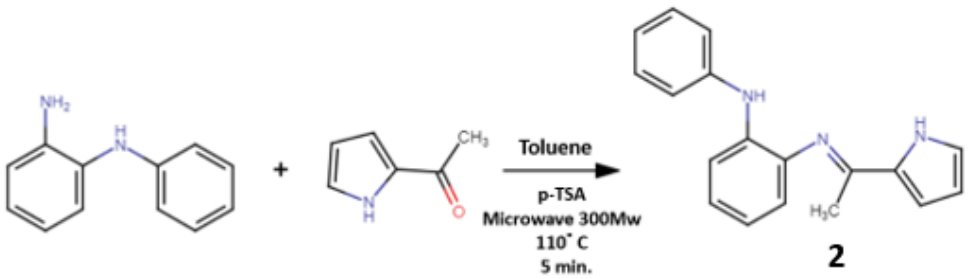
The chemical composition and functional groups of MCs were described by Platinum Attenuated Total Reflectance (ATR) accessories from Bruker Tensor 27 Fourier Transform Infrared Spectroscopy (FTIR). A total of 16 scans were taken. The spectrometer's resolution was 4 cm^{-1}.

3.2 Synthesis of (E)-(Z)-N^1-(1-(1H-pyrrole-2-il) Methylene)-N^2-Phenyl Benzene-1,2-Diamine – Ligand 1



0,47 gram (5mmol) pyrrole 2-carboxyaldehyde and 0,46gram (2,5mmol) 2-Aminodiphenylamine was dissolved in 10 ml ethanol separately. Then, 2-Aminodiphenylamine was added to pyrrole 2-carboxyaldeyhde solution drop by drop. Moreover, 30 mg p-toluenesulfonic acid as a catalyst and 1gram molecular sieve as dryer were added into the mixture and reflaxed for 17 hours under nitrogen atmosphere oxygen and moisture free. The reaction was observed by Thin Layer Chromatography (TLC). The molecular sieve was separated from solution by filtration. After evaporation of solvent, **1** was obtained by crystallization twice from n-hexane solution. The melting point of **1** is 92-93^{0}C. FTIR: ν**(N-H) Ph :** 3381cm^{-1}, ν**(N-H) Pr :** 3154cm^{-1}, ν**(C-H) Ph :** 3065-2851cm^{-1}, ν**(C=N) :** 1609cm^{-1}. ^{1}H-NMR: (500 MHz , d-DMSO) , ppm **δ(-N*H*) Pr** 9.51 (s 1H) , **δ(-N=*C*-*H*)** 8.37 (s 1H), **δ(*C*-*H*) (Pr ve Ph)** 7.32 (m, 3H), 7.21 (m, 2H), 7.11 (m, 2H), 7.0 (d, 2H), 6.87 (t, 1H), 6.72 (d, 1H), 6.35 (t, 1H). ^{13}C-NMR (126 MHz , d-DMSO) , ppm δ(N=***C***-H) 148.4 , δ(***C***-H) (Pr ve Ph) 142.4, 138.6, 138.4, 131.4, 129.3, 126.6, 123.0, 121.7, 119.7, 117.6, 116,6, 114.0, 110.7.

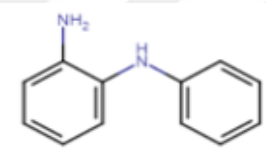
3.3 Synthesis of (E)-(Z)-N^1-(1-(1H-Pirol-2-il) Ethylene)-N^2-Fenil Benzen-1,2-Diamine – Ligand 2



0,54 gram (5 mmol) 2-acetylpyrrole and 0,46 gram (2,5mmol) 2-Aminodiphenylamine were dissolved in 5 ml toluene. Then, 30 mg p-toluenesulfonic acid as a catalyst and

1gram molecular sieve as dryer were added into the mixture and the mixture was put in Microwave reactor in 110^0C for 5 minutes. The reaction was observed by Thin Layer Chromatography (TLC). The molecular sieve was separated from solution by filtration. After evaporation of solvent, **2** was obtained by crystallization twice from n-hexane solution. The melting point of **2** is 78-79^0C. FTIR: ν**(N-H) Ph :** 3357cm^{-1}, ν**(N-H) Pr :** 3299cm^{-1}, ν**(C-H) Ph :** 3061-2873cm^{-1}, ν**(C=N) :** 1617cm^{-1}. ^{1}H-NMR: (500 MHz , d-DMSO) , ppm **δ(-N*H*) Pr** 9.62 (s 1H) , **δ(**-N=*C*-***CH₃*)** 2.26 (s 3H) , **δ(***C*-*H*) **(Pr ve Ph)** 7.35 (m, 3H), 7.28 (m, 2H), 7.14 (m, 2H), 7.04 (d, 2H), 6.95 (t, 1H), 6.88 (d, 1H), 6.73 (t, 1H). ^{13}C-NMR (126 MHz , d-DMSO) , ppm δ(N=***C***-CH3) 159.4 , δ(***C***-H) (Pr ve Ph) 138.1, 138.6, 135.7, 132.7, 129.2, 124.4, 122.0, 121.3, 120.6, 119.7, 119.06, 114.8, 112.6,110.1.

3.4 2-Amino Diphenylamine- Ligand 3



3

The melting point of **2** is 79^0C. FTIR: ν**(N-H) Ph :** 3357cm^{-1}, ν**(N-H-H) Ph :**3300cm^{-1} ,ν**(C-H) Ph :** 3061-2873cm^{-1}. ^{1}H-NMR: (500 MHz , d-DMSO) , **δ(***N-H-H***) (Ph)** 3.55(s 2H), **δ(***N-H***) (Ph)** (s 1H) 9.47 , **δ(***C-H***) (Ph)** 7.54-7.07 (m , 9H). ^{13}C-NMR (126 MHz , d-DMSO) , **δ(*C*-H) (Ph)** 138.1, 138.6, 135.7, 132.7, 129.2, 124.4, 122.0, 121.3, 120.6, 119.7, 119.06, 114.8, 112.6,110.1.

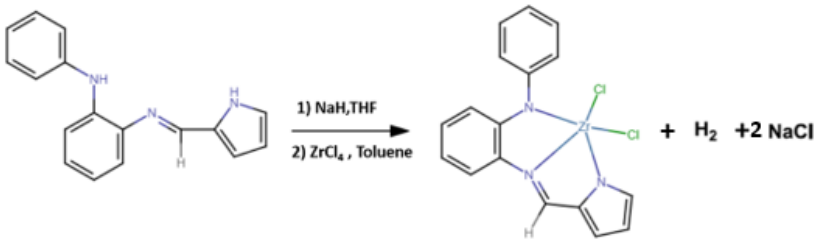
3.5 Synthesis of Complex 1a

1 **1a**

0.1 gram (0.38mmol) Ligand **1** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then, NaH solution

was added to ligand solution drop by drop, stirred for three hours. THF was evaporated and then the solution was put in to freezer to reach -30^{0}C. After that, $TiCl_4$ (0.07 g, 0,38 mmol) was dissolved in 10 ml THF solution and $TiCl_4$ solution was mixed with deprotonated **1** solution .The reaction was stirred and too one day. At the end of the reaction NaCl white was precipitated and filtered from solution by using Celite 545.Toluene was evaporated and the complex material was washed with 10ml n-hexane. 22% yield was obtained. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N=*C-H*) 8.38 (s, 1H), δ(*C-H*) (Pr ve Ph) 7.76 (d, 2H), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H) E/Z . **Complex Ti**: ppm, δ(-N=*C-H*) 8.81 (s, 1H), δ(*C-H*) (Pr ve Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.29 (t, 3H), 7.23 (d, 2H), 7.02 (t, 1H), 6.97 (s, 1H).

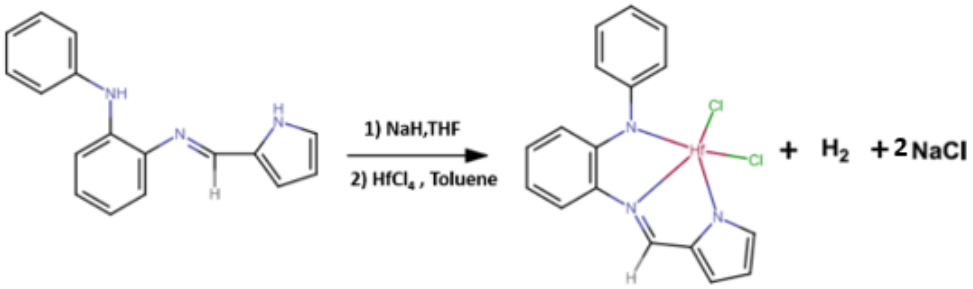
3.6 Synthesis of Complex 1b



1 **1b**

0.1 gram (0.38mmol) Ligand **1** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then, NaH solution was added to ligand solution drop by drop the reaction was completed after three hours.THF was evaporated, then the solution was put in to freezer to reach -30^{0}C. After that, $ZrCl_4$ (0.09 g, 0,38 mmol) was dissolved in 10 ml THF solution and $ZrCl_4$ solution was mixed with deprotonated **1** ligand solution .The reaction was stirred and too one day. In the end of the reaction NaCl white was precipitated and seperated from solution by using Celite 545.THF was evaporated and the complex material was washed with 10ml n-hexane. 40% yield was found. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N=*C-H*) 8.38 (s, 1H), δ(*C-H*) (Pr ve Ph) 7.76 (d, 2H), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H) E/Z isomerism. **Complex Zr**: ppm, δ(-N=*C-H*) 8.81 (s, 1H), δ(*C-H*) (Pr ve Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.29 (t, 3H), 7.23 (d, 2H), 7.02 (t, 1H), 6.97 (s, 1H).

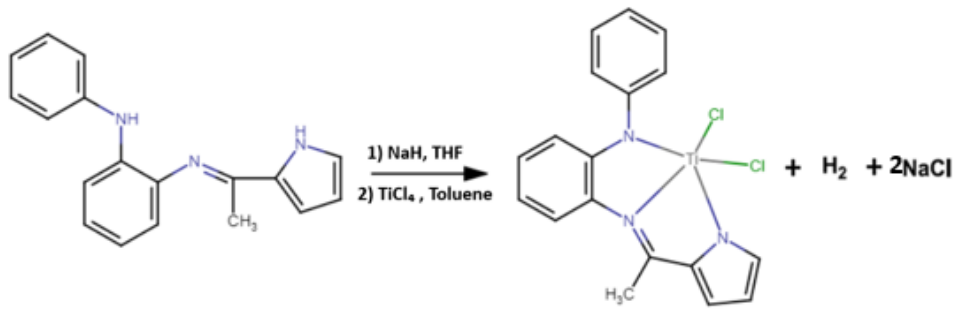
3.7 Synthesis of Complex 1c



1 **1c**

0.1 gram (0.38mmol) Ligand **1** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then, NaH solution was added to ligand solution drop by drop, stirred for three hours. THF was evaporated and, then the solution was put in to freezer to reach -30^{0}C. After that, $HfCl_4$ (0.12 g, 0,38 mmol) was dissolved in 10 ml THF solution and $HfCl_4$ solution was mixed with deprotonated ligand **1** solution .The reaction was stirred and too one day. In the end of the reaction NaCl white was precipitated and seperated from solution by using Celite 545.THF was evaporated and the complex material was washed with 10ml n-hexane. 33% yield was found. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N=*C-H*) 8.38 (s, 1H), δ(*C-H*) (Pr ve Ph) 7.76 (d, 2H), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H) E/Z isomerism. **Complex Hf**: ppm, δ(-N=*C-H*) 8.81 (s, 1H), δ(*C-H*) (Pr ve Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.29 (t, 3H), 7.23 (d, 2H), 7.02 (t, 1H), 6.97 (s, 1H).

3.8 Synthesis of Complex 2a



2 **2a**

0.1 gram (0.38mmol) Ligand **2** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then, NaH solution

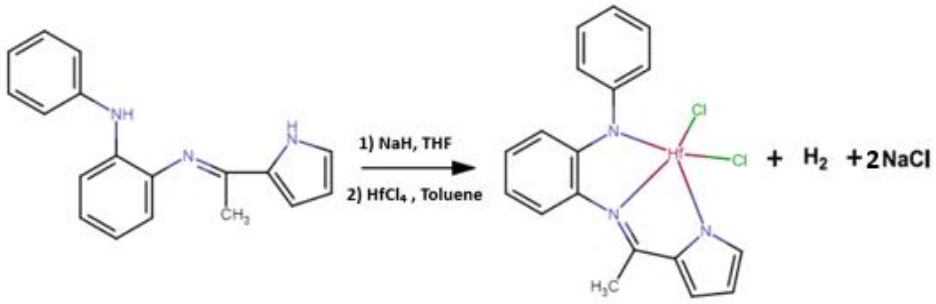
was added to ligand solution drop by drop, stirred for three hours. THF was evaporated and, then the solution was put in to freezer to reach -30^{0}C. After that, $TiCl_4$ (0.09 g, 0,38 mmol) was dissolved in 10 ml THF solution and $TiCl_4$ solution was mixed with deprotonated ligand **2** solution .The reaction was stirred and too one day. At the end of the reaction NaCl white was precipitated and seperated from solution by using Celite 545.THF was evaporated and the complex material was washed with 10ml n-hexane. 10% yield was found. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N=*C*-***H***) 8.38 (s, 1H), δ(*C*-***H***) (Pr ve Ph) 7.76 (d, 2H), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H) **,** δ **(**-N=*C*-***CH₃*****)** 2.28 (s 3H) E/Z isomerism.. **Complex Ti**: ppm, δ(-N=*C*-***H***) 8.81 (s, 1H), δ(*C*-***H***) (Pr ve Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.29 (t, 3H), 7.23 (d, 2H), 7.02 (t, 1H), δ **(**-N=*C*-***CH₃*****)** 2.28 (s 3H).

3.9 Synthesis of Complex 2b

2 **2b**

0.1 gram (0.38mmol) Ligand **2** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then, NaH solution was added to ligand solution drop by drop, stirred for three hours. THF was evaporated, then the solution was put in to freezer to reach -30^{0}C. After that, $ZrCl_4$ (0.09 g, 0,38 mmol) was dissolved in 10 ml THF solution and $ZrCl_4$ solution was mixed with deprotonated ligand **2** solution .The reaction was stirred and too one day. At the end of the reaction NaCl white was precipitated and seperated from solution by using Celite 545.THF was evaporated and the complex material was washed with 10ml n-hexane. 22% yield was found. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N=*C*-***H***) 8.38 (s, 1H), δ(*C*-*H*) (Pr ve Ph) 7.76 (d, **2H**), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H), δ **(**-N=*C*-***CH₃*****)** 2.28 (s 3H) E/Z isomerism.. **Complex Zr**: ppm, δ(-N=*C*-***H***) 8.81 (s, 1H), δ(*C*-***H***) (Pr ve Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.29 (t, 3H), 7.23 (d, 2H), 7.02 (t, 1H), δ **(**-N=*C*-***CH₃*****)** 2.28 (s 3H).

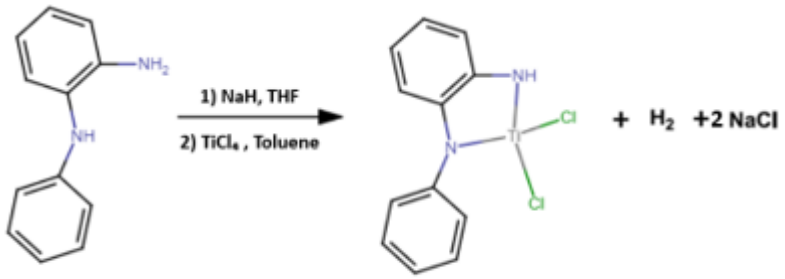
3.10 Synthesis of Complex 2c



2 **2c**

0.1 gram (0.38mmol) Ligand **2** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then, NaH solution was added to ligand solution drop by drop, stirred for three hours. THF was evaporated and, then the solution was put in to freezer to reach -30^{0}C. After that, $HfCl_4$ (0.07 g, 0,38 mmol) was dissolved in 10 ml toluene solution and $HfCl_4$ solution was mixed with deprotonated ligand **2** solution .The reaction was stirred and too one day. In the end of the reaction NaCl white was precipitated and seperated from residue by using Celite 545.THF was evaporated and the complex material was washed with 10ml n-hexane. 17% yield was found. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N=*C*-***H***) 8.38 (s, 1H), δ(*C*-***H***) (Pr ve Ph) 7.76 (d, 2H), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H), δ **(**-N=*C*-***CH$_3$)*** 2.28 (s 3H) E/Z isomerism. **Complex Hf**: ppm, δ(-N=*C*-*H*) 8.81 (s, 1H), δ(*C*-*H*) (Pr ve Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.29 (t, 3H), 7.23 (d, 2H), 7.02 (t, 1H), δ **(**-N=*C*-***CH$_3$)*** 2.28 (s 3H).

3.11 Synthesis of Complex 3a

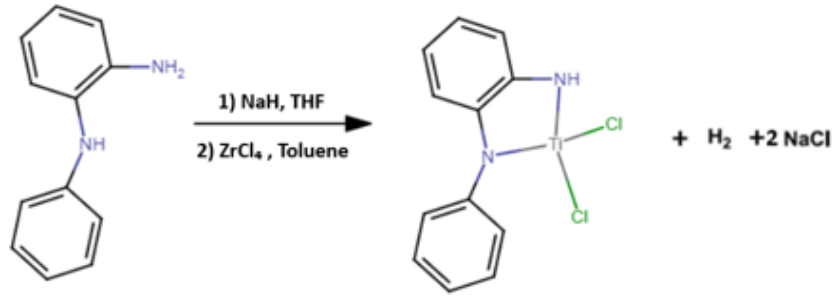


3 **3a**

0.065 gram (0.38mmol) Ligand **3** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then

NaH solution was added to ligand solution drop by drop, stirred for three hours. THF was evaporated and, then the solution was put in to freezer to reach -30^{0}C. After that, $TiCl_4$ (0.07 g, 0,38 mmol) was dissolved in 10 ml THF solution and $TiCl_4$ solution was mixed with deprotonated ligand **3** solution .The reaction was stirred and too one day. At the end of the reaction NaCl white was precipitated and seperated from solution by using Celite 545.THF was evaporated and the complex material was washed with 10ml n-hexane. 65% yield was found. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N-***H***) 3.51 (s, 1H), δ(*C*-***H***) (Pr-Ph) 7.76 (d, 2H), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H). **Complex Ti**: ppm, δ(-N-***H***) 5.82 (s, 1H), δ(*C*-***H***) (Pr - Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.23 (d, 2H), 7.02 (t, 1H), 6.97 (s, 1H).

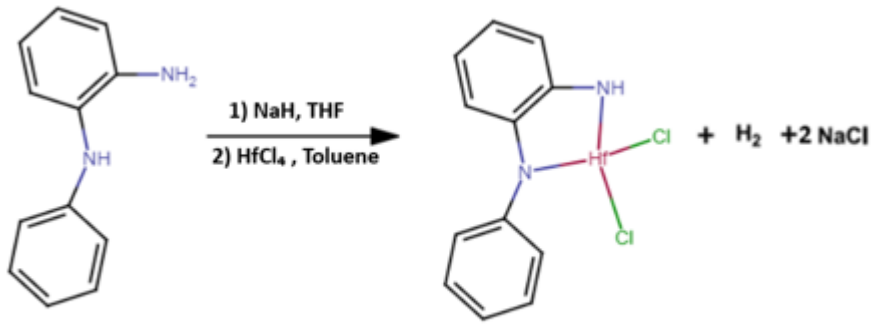
3.12 Synthesis of Complex 3b



3 **3b**

0.065 gram (0.38mmol) Ligand **3** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then, NaH solution was added to ligand solution drop by drop, stirred for three hours. THF was evaporated and, then the solution was put in to freezer to reach -30^{0}C. After that, $ZrCl_4$ (0.09 g, 0,38 mmol) was dissolved in 10 ml toluene solution and $ZrCl_4$ solution was mixed with deprotonated ligand **3** solution .The reaction was stirred and too one day. In the end of the reaction NaCl white was precipitated and seperated from solution by using Celite 545.THF was evaporated and the complex material was washed with 10ml n-hexane. 70% yield was found. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N-*H*) 3.51 (s, 1H), δ(*C*-*H*) (Pr-Ph) 7.76 (d, 2H), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H). **Complex Ti**: ppm, δ(-N-***H***) 5.82 (s, 1H), δ(*C*-***H***) (Pr - Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.23 (d, 2H), 7.02 (t, 1H), 6.97 (s, 1H).

3.13 Synthesis of Complex 3c



3 **3c**

0.065 gram (0.38mmol) Ligand **3** was dissolved in 5ml THF.Then, 0.03gram (0.76mmol) NaH (%60 of mineral oil) was dissolved in 5ml THF separately. Then NaH solution was added to ligand solution drop by drop, stirred for three hours. THF was evaporated and, then the solution was put in to freezer to reach -30^{0}C. After that, $HfCl_4$ (0.12 g, 0,38 mmol) was dissolved in 10 ml toluene solution and $HfCl_4$ solution was mixed with deprotonated **3** ligand solution .The reaction was stirred and too one day. At the end of the reaction NaCl white precipitate salt occured and seperated from residue by using Celite 545.Toluene was evaporated and the complex material was flushed with 10ml n-hexane. 62% yield was obtained. 1H-NMR:(500 MHz, d-acetone)- **Ligand Na**: ppm, δ(-N-***H***) 3.51 (s, 1H), δ(*C*-***H***) (Pr-Ph) 7.76 (d, 2H), 7.63 (m, 4H), 7.47 (m, 4H), 7.21 (t, 3H), 7.06 (t, 2H), 6.92 (m, 2H). **Complex Ti**: ppm, δ(-N-***H***) 5.82 (s, 1H), δ(*C*-***H***) (Pr - Ph) 7.84 (m, 2H), 7.57 (m, 1H), 7.45 (t, 2H), 7.23 (d, 2H), 7.02 (t, 1H), 6.97 (s, 1H).

4. RESULTS AND DISCUSSION

4.1 Characterization of the Schiff Base Ligands

Non-symmetrical pyrrole-imine ligands were synthesized and different synthesis approachs were used such as microwave in order to reach substance with high yield [33]. By Using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods non-symmetrical pyrrole-imines were analysized. Using an n-hexane solution at 263 K, single crystals of 2-aminodiphenylamine were obtained and characterized using X-ray diffraction.

From its spectral details, the structure of 2-aminodiphenylamine has been identified. The structure determination method was described in detail below.

The molecular structure of 2-aminodiphenylamine was shown in Figure 4.1. The crystallographic data were listed in Table 4.1.

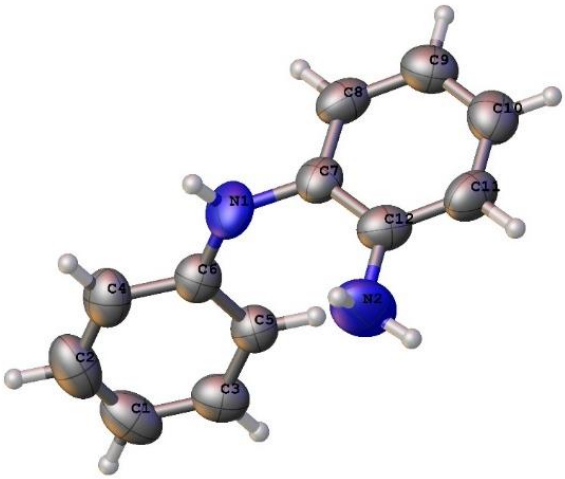


Figure 4.1 : Molecular structure of 2-aminodiphenylamine.

Table 4.1 : Sample and Crystal of 2-aminodiphenylamine.

Identification code	2-aminodiphenylamine
Formula weight	275.34
Crystal system	monoclinic
Space group	P21/n
a/A	107555(16)
b/A	5.8257(9)
c/A	15.636(2)
ts/A	5.8257(9)
c/A	15.636(2)
al°	90
6/'	96.093(4)
VP	90
Volume/A^3	974.2(2)
Z	4
OcaocCl/CM^3	1.877
F(000)	584.0
Crystal size/mm^3	0.500 x 0.100 s 0.050
Radiation	Moka(a (λ= 0.71073)
2Θ range for data collection	4.388 to 49.964
Reflections collected	35573
Data/restraints/parameters	1711/0/140
Goodness-of-fit on F^2	1.064
Final R Indexes fl>=2σ	R1= 0.0499. wR2 = 0.0796
Final R indexes fall data)	R1= 0.1353. wR2: = 0.1052
Largest dig. pealdboie / e A•^{3}	0.11/-0.12

With respect to the ^{1}H-NMR spectrum of **1**, the imine proton, (-*H*C=N), was appeared at 8.37 ppm. Phenyl and pyrrole protons (12 H) appeared at 7.32- 6.35 ppm (Figure 4.2). The ^{1}H-NMR data of **1-3** were given in Table 4.2.

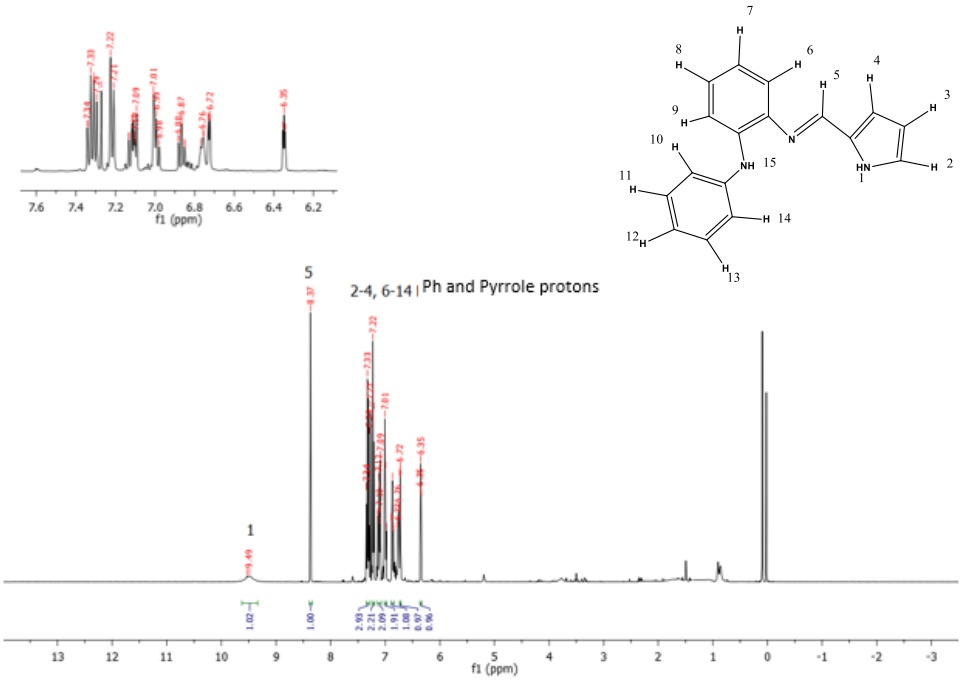


Figure 4.2 : ^{1}H-NMR spectrum of **1**.

Table 4.2 : ^{1}H-NMR spectral data (ppm) of ligands **1-3**.

Ligand	δ(-NH)Pr	δ(-N=C-H)	δ(-CH) Pr-Ph	δ(-NH)Ph	δ(-N=C-CH₃)
1	9.51 (s, 1H)	8.37 (s 1H)	7.32 (m 3H), 7.21 (m,2H), 7.11 (m,2H), 7.0 (d,2H), 6.87(t,1H), 6.72 (d,1H), 6.35(t, 1H)	5,5 (s,1H)	-
2	9.62 (s, 1H)		7.35 (d,3H), 7.28(m,2H), 7.14 (d,2H), 7.04 (t,2H), 6.95(t,2H), 6.88 (t,1H), 6.73(m, 2H) 6.31(t,1H)	5.84 (s,1H)	2.26 (sd,3H)
3	-	-	7.54-7.07 (s,9H)	9.47 (s,1H), 3.55(s,2H)	-

With respect to the ^{13}C-NMR spectrum of **1**, - (H)*C*=N imine carbon was appeared at 148.4 ppm, the pyrrole carbons were appeared at 142.2,138.6,138.4,131.4 ppm. The phenyl carbons were observed 129.3,126.6,123,121.7,119.7,117.6,116.6,114,110.7 ppm (Figure 4.3). The ^{13}C-NMR data of **1-2** ligands were given in Table 4.3.

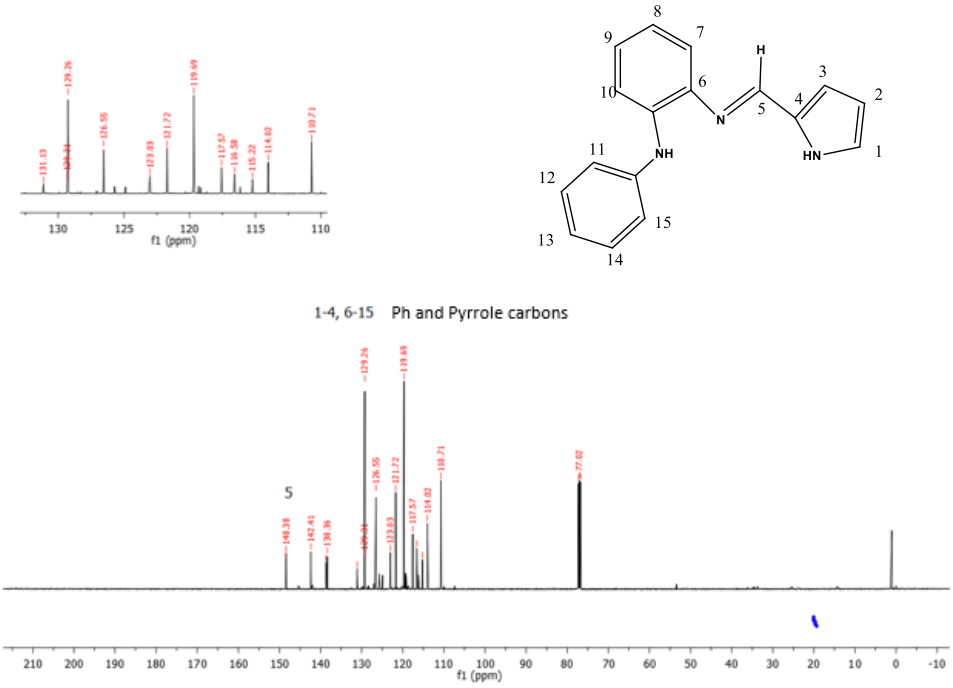


Figure 4.3 : ^{13}C- NMR spectrum of Ligand **1.**

Table 4.3 : ^{13}C-NMR spectral data (ppm) of compounds **1-2**.

Compound	δ(-N=C-H)	δ(-N=C-CH₃)	δ(-CH) Pr-Ph	δ(-N=C-CH₃)
1	148.4		142.4, 138.6, 138.4,131.4,129.3,126.6,123, 121.7, 119.7, 117.6,116.6,114,110.7	
2		159.4	138.1, 135.7, 132.7,129.4,126.6,,123, 121.7, 119.7, 119.06,114.8,112.6,110.1	16.8

With respect to the FT-IR spectrum of **1** ν(N-H)Ph streching band was seen at 3388 cm^{-1}, the ν(N-H)Pr streching band was seen at 3154 cm^{-1}. ν(C-H)Ph appeared in range of 3065-2851 cm^{-1} , while 2-pyrrole **c**arboxyaldehyde ν(C=O) 1626 cm^{-1} was

disappeared, ν(C=N)Ph appeared in 1609 cm^{-1}. (Figure 4.4 and Figure 4.5). The FTIR data of Ligand **1-3** were given in Table 4.4.

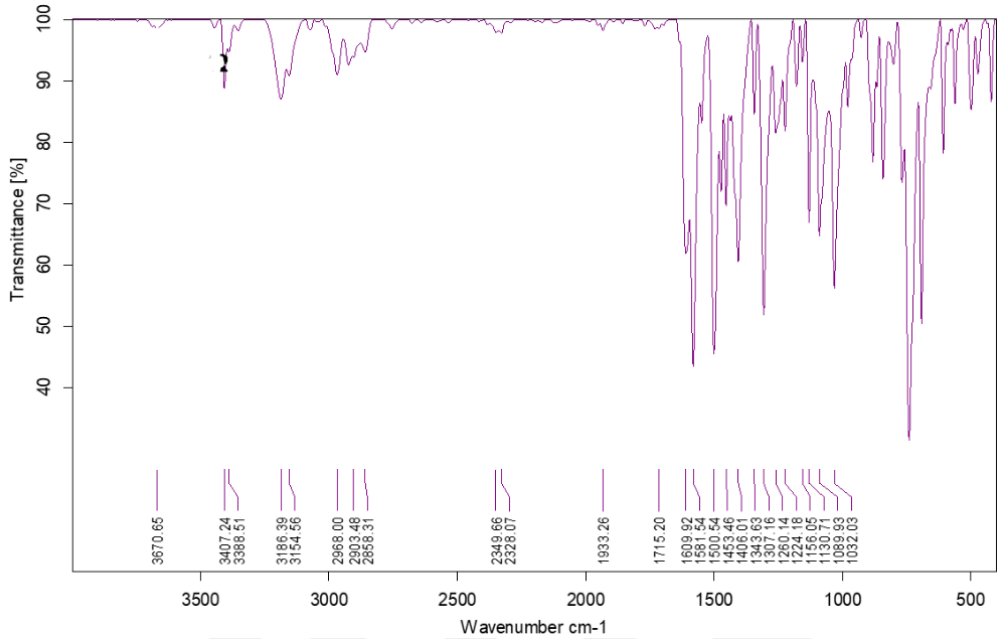


Figure 4.4 : FT-IR spectrum of Ligand **1**.

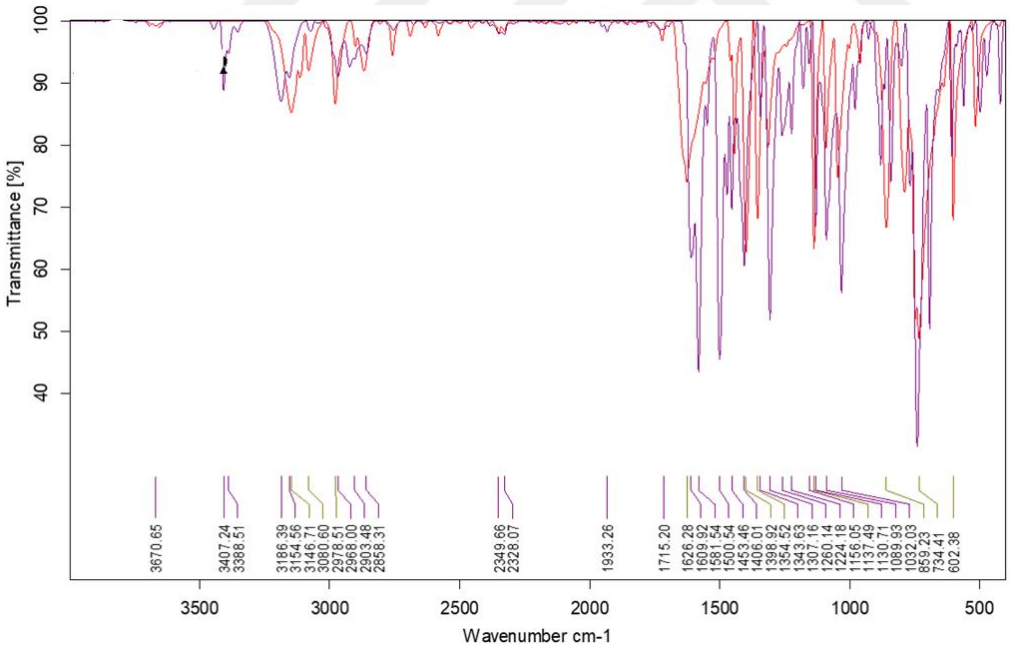


Figure 4.5 : FT-IR spectrum of Ligand **1** with pyrrole 2-carboxyaldehyde.

Table 4.4 : Data spectrum of FT-IR of (cm^{-1}) of compounds **1-3**.

Ligand	ν(N-H) Ph	ν(N-H) Pr	ν(C-H) Ar	ν(C=N)	ν(N-HH) Ph
1	3388	3154	3065-2851	1609	
2	3357	3299	3061-2873	1617	
3	3288	-	-	-	3442-3360

4.2 Characterization of 1a-1c, 2a-2c, 3a-3c

The reaction mechanism of **1a-1c, 2a-2c** and **3a-3c** complexes was told in section 3. First of all, Ligands were characterized and evaluated in term of yield with their spectroscopic analysis.

For instance, after synthesis of Ligand **1**, the ligand was deprotonated with sodium hydride. This deprotonation step is very crucial for insertion of ligand to metal ion. After deprotonation, the ligand hydrogens was disappeared in ^{1}H-NMR. Then, cooled deprotonated ligand was reacted with $ZrCl_4$ metal salt and the color changed to yellowish to black and the complex **1a** synthesis was completed.

Zirconium metal complex **2b** has been told as a example of all complexation mechanism. The reason is that Ti, Zr and Hf mechanisms are very similar.

Through the chelation of **1** and **2** to the metal center to five member chelation ring were observed. It adds extra stability to complexes.

With respect to the ^{1}H-NMR data of **1b**, the wide band of **δ(**-N-***H*****) Pr** at 9.87 ppm disappeared. **δ(**C-***H*****) (Pr and Ph) (12H)** protons shifted to upfield and seen at 7.84 and 6.95 ppm. **δ(**-N=C-***H*****)** protons indicated a important change and shifted from 8.29 to 8.81 ppm (Figure 4.5).

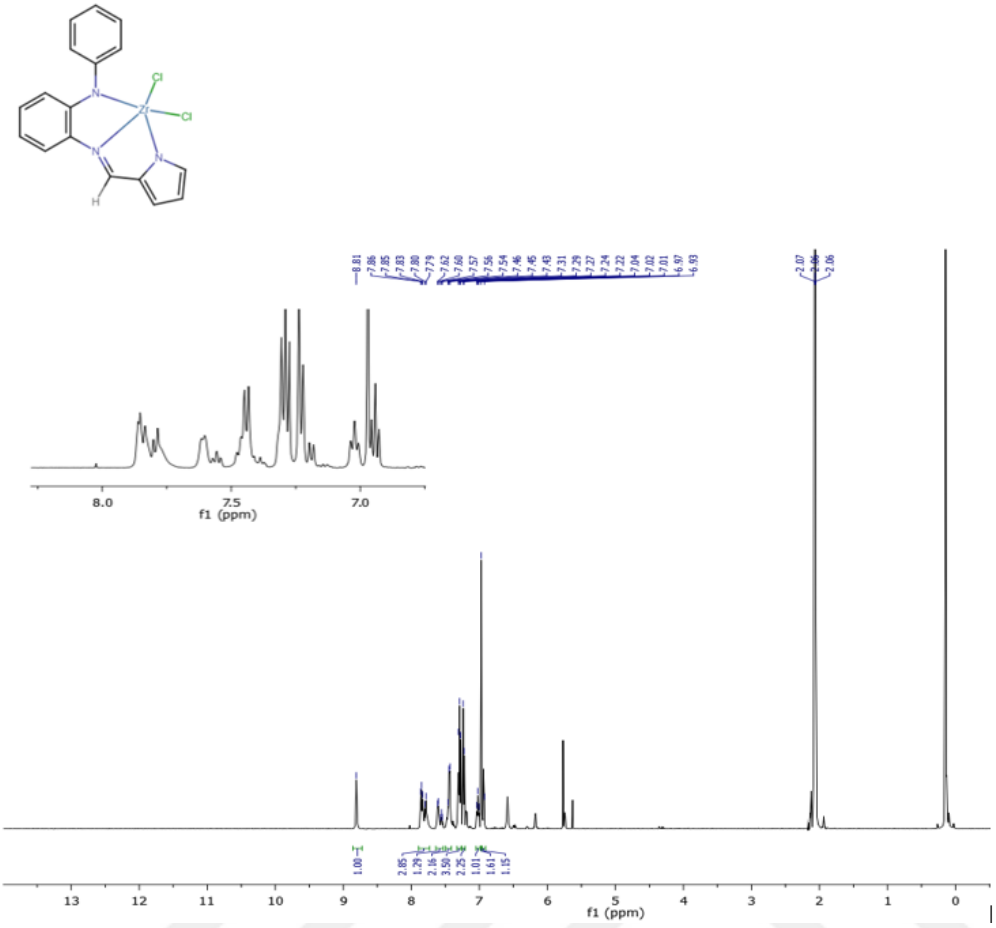


Figure 4.6 : ^{1}H- NMR spectum of **1b**.

With respect to the ^{1}H-NMR data of **2b**, the band of **δ(-N*H*) Pr** at 9.71 ppm disappeared. **δ(*C*-*H*) (Pr and Ph)** protons shifted to upfield and seen at 7.34 and 7.55 ppm. **δ(-N=*C*-CH_3)** protons indicated in 2.31 ppm (Figure 4.6).

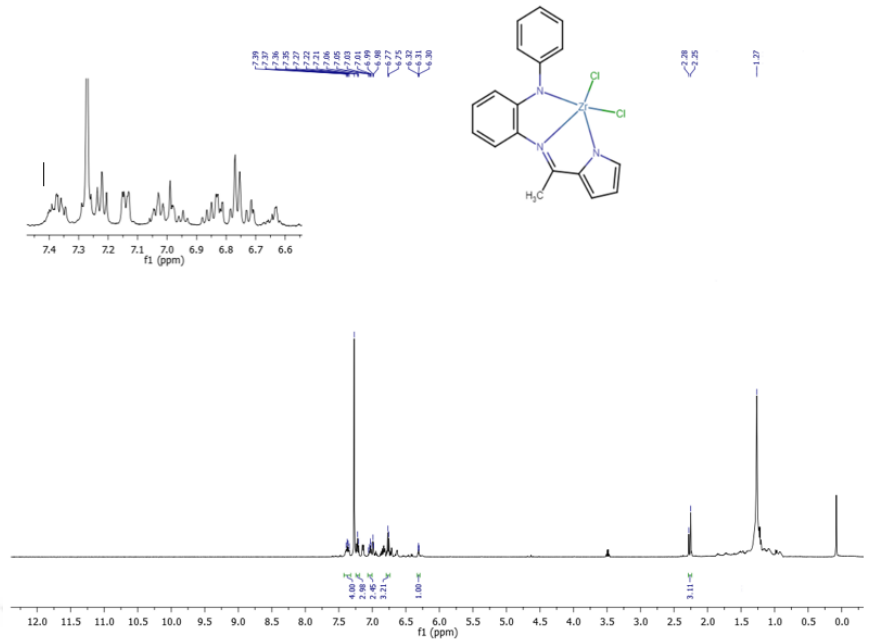


Figure 4.7 : ^{1}H-NMR spectum of **2b**.

With respect to the ^{1}H-NMR data of 3a, the band of **δ(-N*H*) NH$_2$** at 9.71 ppm disappeared. **δ(*C*-*H*) (Ph)** protons shifted to upfield and seen at 6.3 and 6.45 ppm. **δ(-N-H)** protons indicated in 5.82 ppm (Figure 4.8).

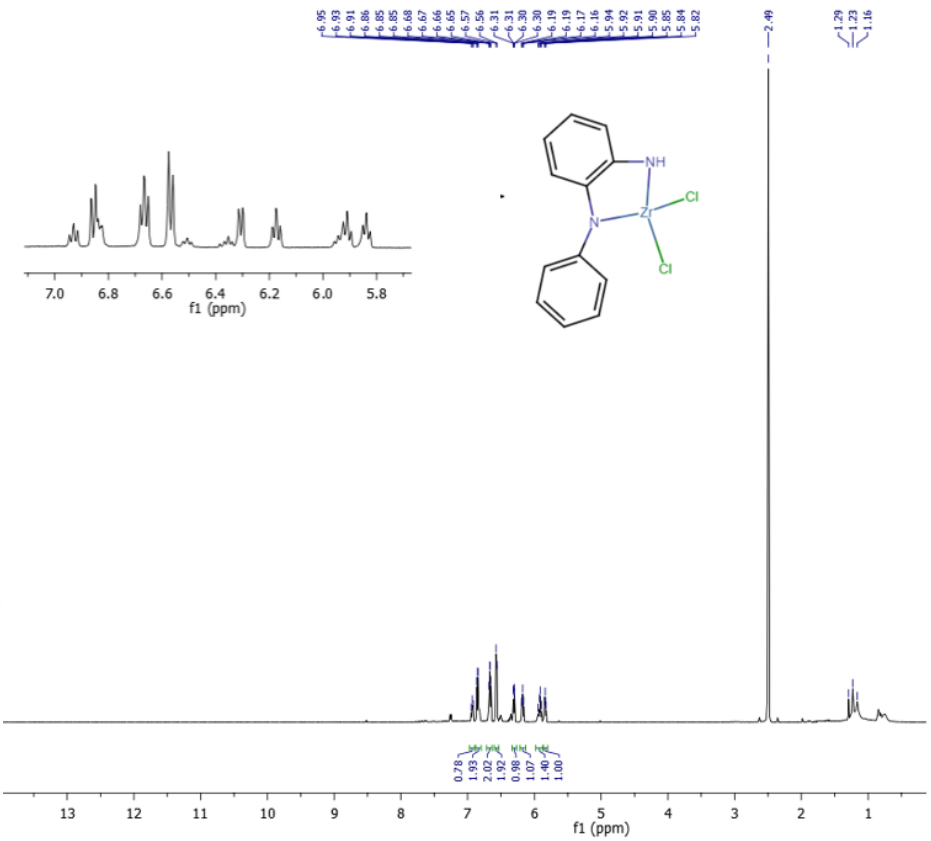


Figure 4.8 : ^{1}H- NMR spectum of **3b**.

Through the chelation of 1 and 2 to the metal center to five member chelation ring were observed. It adds extra stability to complexes. In 3 , amine nitrogens coordinated to metal and five member chelate occured.

5. CONCLUSION

Electronically flexible nonsymmetic ligands and their group IVB transition metal complexes were synthesized in order to be used as catalyst in olefin polymerization.

Moreover, ethylene polymerization process have been given the name of fundamentally active ligands. Usually, fundamentally active ligands have well-balanced electron donating and withdrawing properties, which are supposed to speed up ethylene polymerization process (evidenced by a slight energy difference between HUMO and LUMO).

The focus of this thesis was to design and prepare a new series of nonsymmetric pyrrole-imine derivate ligands, named **1-3**. They were then used to prepare novel group IVB metal [M = Ti; (a), Zr; (b), Hf; (c)] complexes, named **1a-1c, 2a-2c** and **3a-3c**. The complexes in turn can be used as olefin polymerization catalysts.Using the following spectroscopic techniques, nonsymmetric pyrrole-imine structures and derivative ligands (**1-3**) were found; FT-IR,^{1}H-NMR and ^{13}C-NMR. Using the single crystal X-ray diffraction process, 2-aminodiphenylamine was also described.

Both spectroscopic data revealed that through the nitrogen and pyrrole nitrogen donor atoms of the ligand, the chelation of the non symmetric pyrrole-imine derivative ligands to the metal center took place.

The energy difference between HUMO and LUMO for ligands containing pyrrole-imine derivatives was calculated with Gaussian 09 program using the DFT (Density Functional Theory) BP86 functional def2-SVP basis set and the results are given in Figure 5.1. DFT calculations show that the energy difference between HUMO and LUMO ligands 1-2 is smaller than the Cp (C_5H_5) ligand. Therefore, the first promising data was obtained theoretically that these ligands could electronically flexible for an olefin polymerization catalyst.

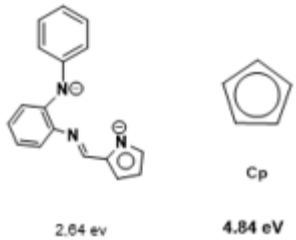


Figure 5.1 : Energy difference between initial ligand and Cp (C_5H_5).

All the spectroscopic evidence proved that the chelation of the nonsymmetric furanimine derivate ligands to the metal center occurred via imine nitrogen and pyrrole nitrogen donor atoms of the ligand.

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APPENDICES

APPENDIX A: Supporting information of results and discussion.

APPENDIX A

Table A.1 : Bond lengths (Å) for 3.

Atom	Length/Å	Atom	Length/Å
C2-C1	1.25(2)	C2-C3	1.37(2)
C4-C3	1.40(2)	C4-C5	1.391(19)
C6-C7	1.24(2)	C6-C11	1.46(2)
C8-C7	1.48(2)	C8-C9	1.26(3)
C10-C9	1.43(2)	C11-C10	1.346(19)
C12-C13	1.49(2)	C12-C14	1.59(2)
C12-C15	1.44(2)	N1-C1	1.382(19)
N1-C4	1.306(17)	N2-C5	1.273(16)

Table A.2 : Bond angles (°) for 3.

Atom	Angle/˚	Atom	Angle/˚
C2-C1-N1	111.6(15)	C1-C2-C3	107.2(15)
C2-C3-C4	107.4(17)	C5-C4-C3	126.4(15)
N1-C4-C3	106.0(14)	N1-C4-C5	127.4(14)
N2-C5-C4	126.8(14)	C7-C6-C11	122.0(14)
C7-C6-N2	122.0(14)	N2-C6-C11	115.7(12)
C6-C7-C8	121.9(16)	C9-C8-C7	115.5(18)
C8-C9-C10	125.1(18)	C11-C10-C9	118.3(15)
C10-C11-C6	116.6(13)	C10-C11-N3	126.3(14)
N3-C11-C6	117.1(13)	C13-C12-C14	107.0(13)
C15-C12-C13	113.6(15)	C15-C12-C14	109.7(13)
N3-C12-C14	104.5(13)	C4-N1-C1	107.5(13)
C5-N2-C6	122.2(12)	C11-N3-C12	126.5(12)

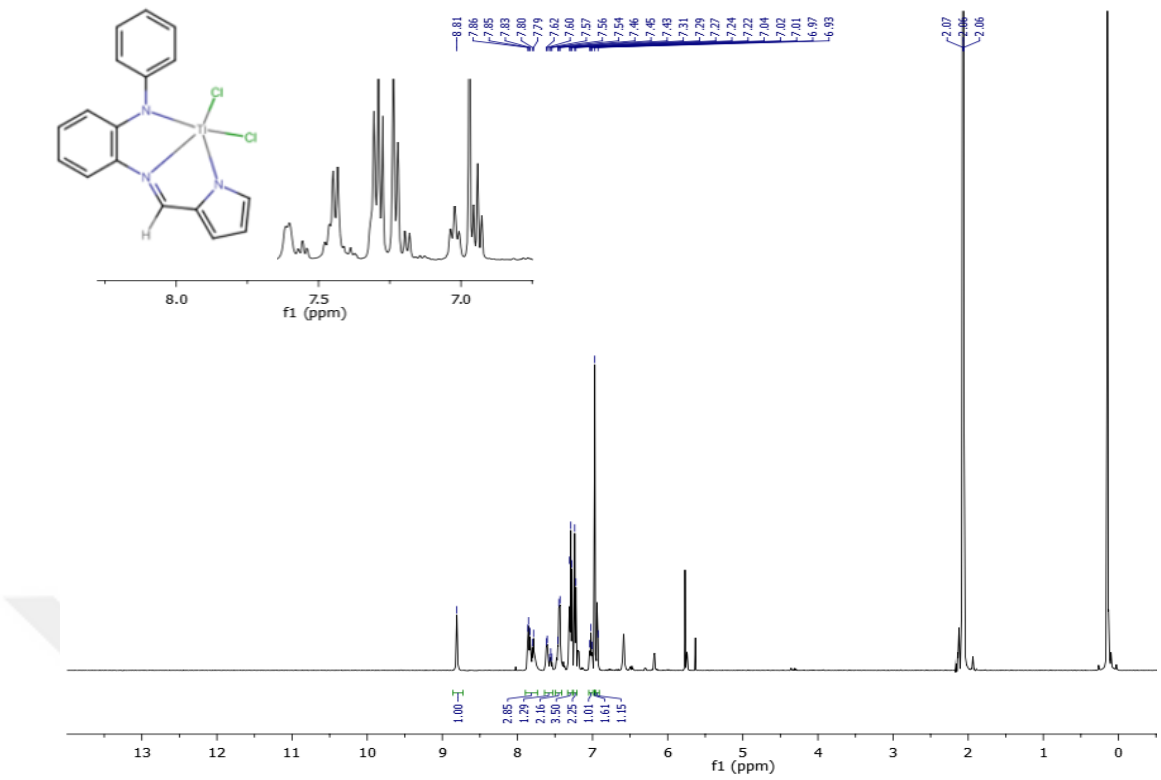

Figure A.1 : ^{1}H- NMR spectum of complex 1a.

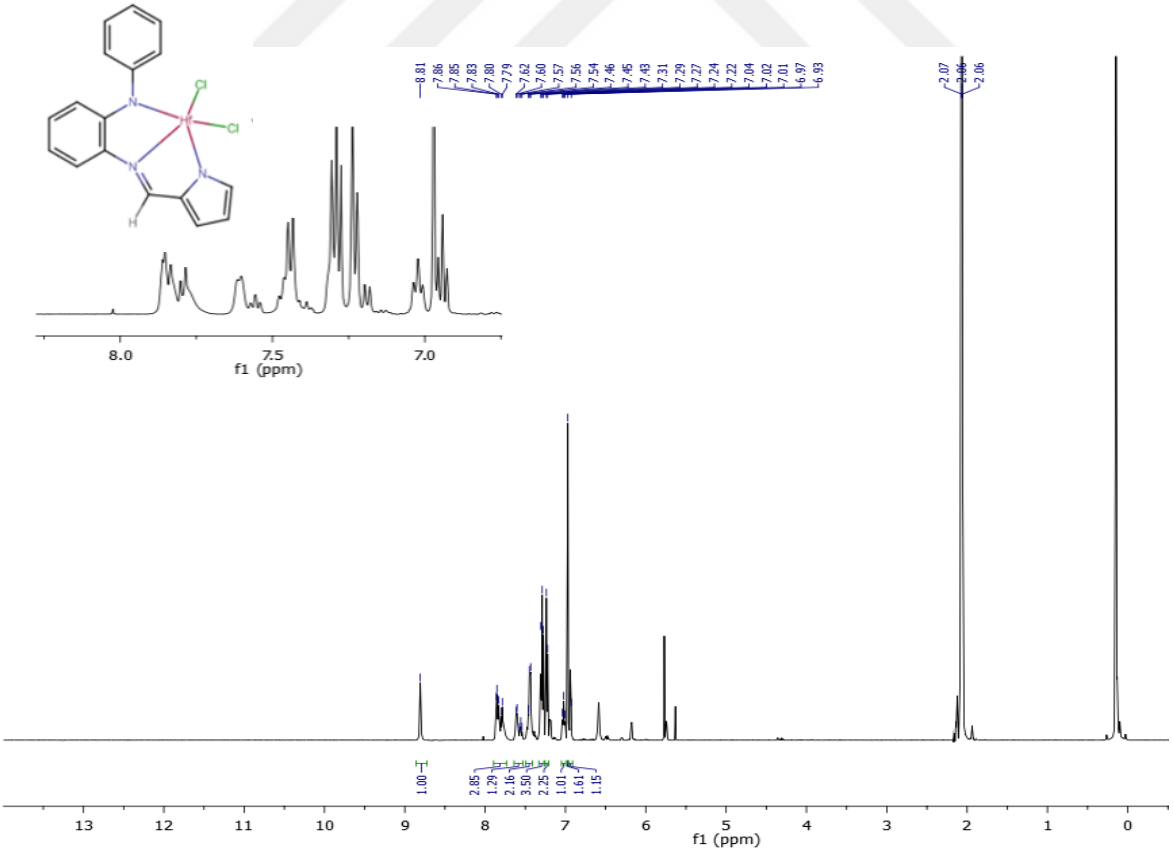

Figure A.2 : ^{1}H-NMR spectum of complex 1c.

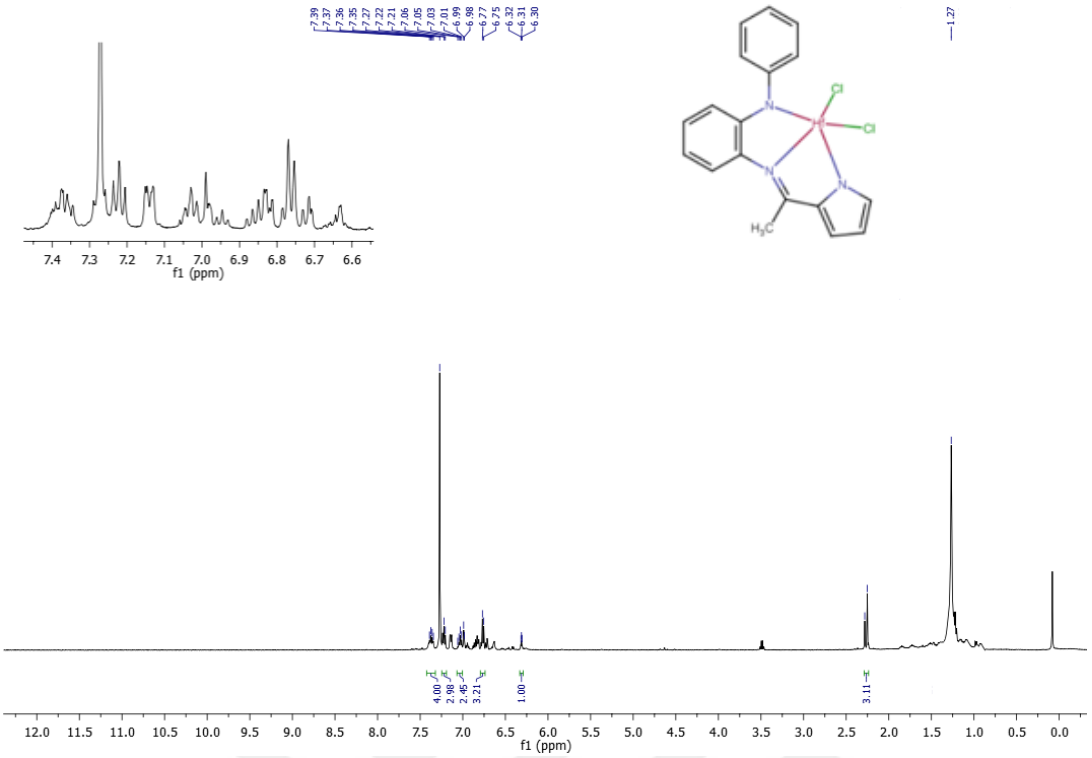

Figure A.3 : ^{1}H- NMR spectum of complex 2a.

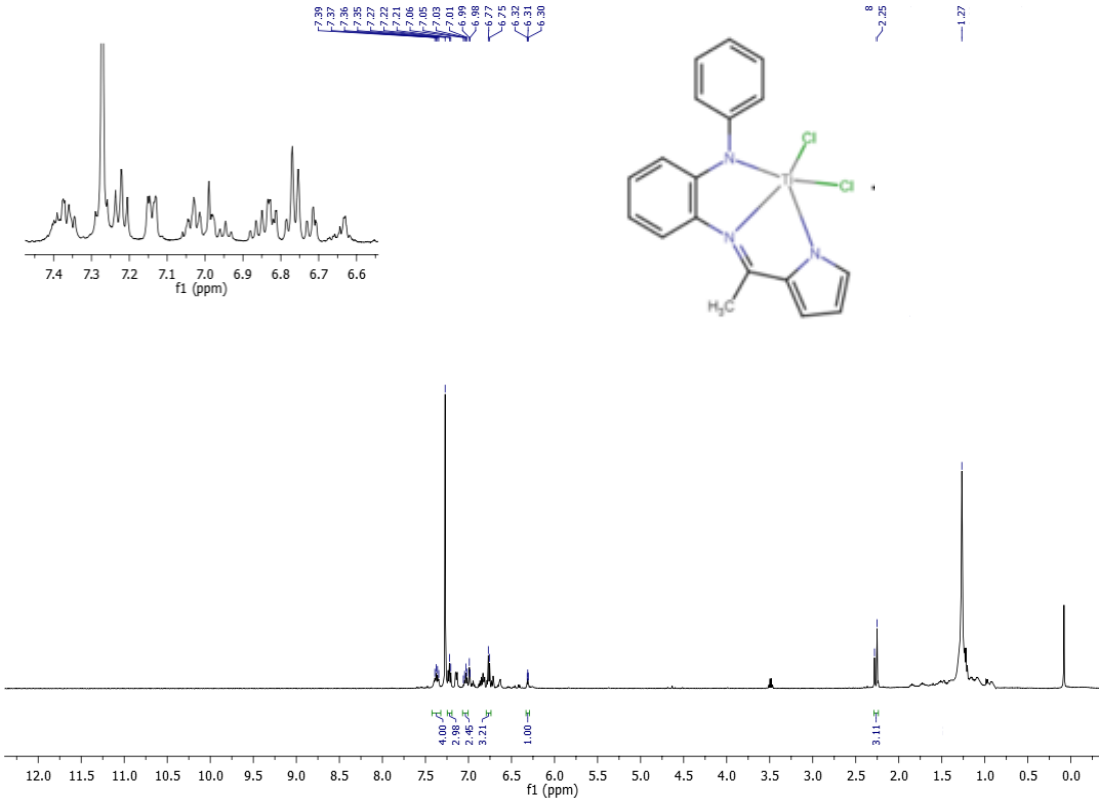

Figure A.4 : ^{1}H- NMR spectum of complex 2c.

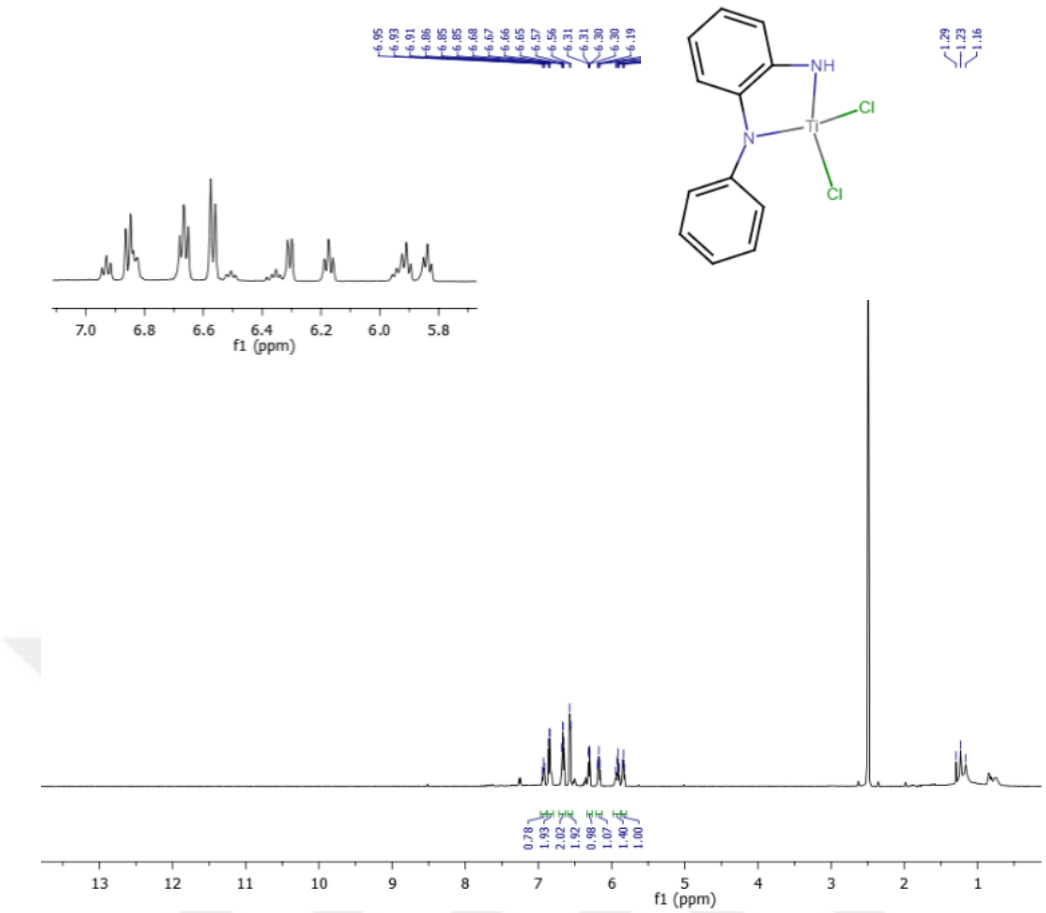

Figure A.5 : ^{1}H- NMR spectum of complex 3a.

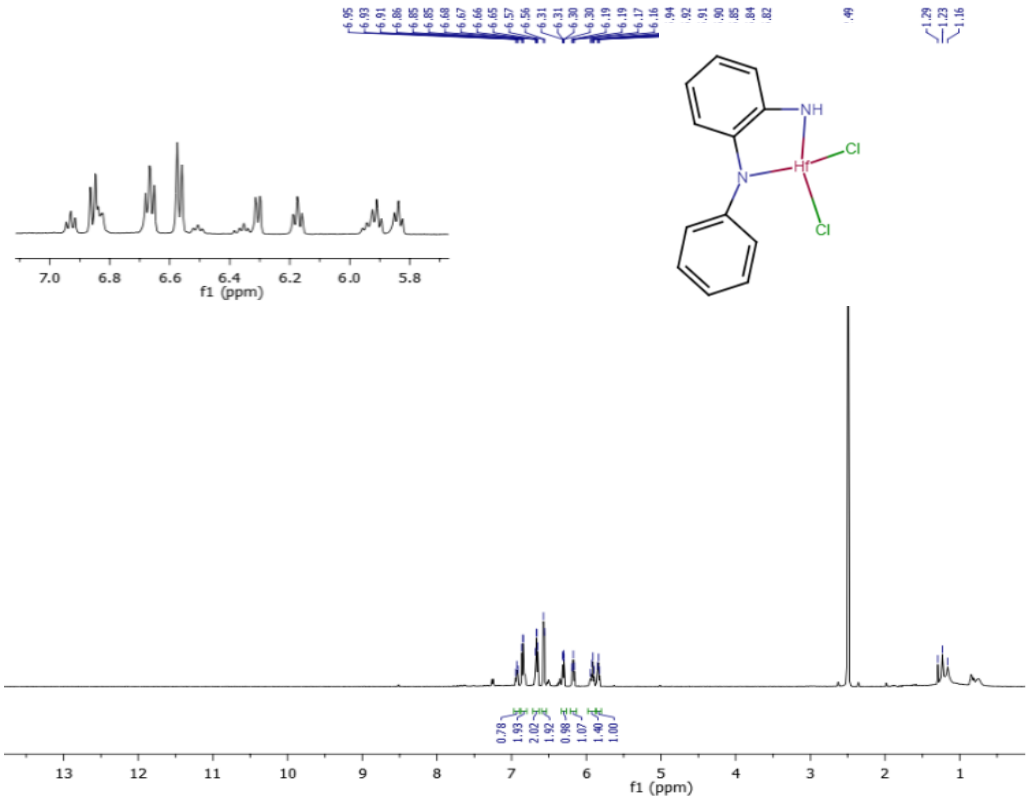

Figure A.6 : ^{1}H- NMR spectum of complex 3c.

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