Synthesis and Screening of Olefin Polymerization Catalysis using Two Aniline Derivatives

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ABSTRACT
Polyethylene has emerged as the most important polyolefin plastic due to its superior mechanical, processing, and chemical stability. The purpose of this research is to investigate the efficacy of a variety of two similar pre-catalysts in the production of either oligomeric or polymeric products. Each pre-catalyst is based on a distinct aniline compound (2,4,6-trimethylaniline & 2,6-dimethylaniline). Three steps make up the polymerization reaction. The ligand synthesis, complex synthesis, and ethylene polymerization were the three steps involved. The ease of production of each catalyst was measured by comparison of the separate yields of each step of the synthesis, following which ethylene polymerization was undertaken culminating in a comparison between the yields of polymer produced for each pre-catalyst. Overall, it was determined that 2,6-dimethylaniline and 2,4,6-trimethylaniline produced polymeric product. Further to this, the pre-catalyst synthesized from 2,6-dimethylaniline showed the highest polymer yield.
Keywords: Ethylene polymerization, catalysts, ligand, polymer.

1. INTRODUCTION

Plastics are an essential part of daily life, both in their preparation and, in part, because of the numerous recycling options that benefit from effective catalysts (Schoeneberger & Luinstra, 2021). Polyethene is the most important and widely used plastic on a global scale. It is the most common industrial polymer, with an annual production of 80 million tons, and is produced by polymerization of ethylene (Nazeeha Alkayal, 2016). Polyethene-based materials are very important in modern life because of their high recycling, good barrier properties, low cost, and chemical resistance to various solvents. They cover a wide range of applications from commodity plastics to precision processed biomaterials. Polyethylene comes in three main forms that together produce over 80 million tons of the plastic every year. Low density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) are the most used as electrical insulation and in film packaging, while high density polyethylene is more rigid and can be blown into containers for household chemicals such as bleach or washing up liquid, as well as in industrial packaging. The development of new transition metal catalysts has played a significant role in

the fast-growing polyolefins industry. Catalyst development has frequently resulted in the development of new, better performing, less expensive polyolefins (Zohuri *et al.,* 2014). As is well-known, most polyolefinic materials are produced using transition metal-catalyzed olefin polymerization technology. Recently much attention has been paid to the non-metallocene catalysts (Bennett & Schiffino, 2000). This is because complex catalysts have unique properties for producing new polymers that aren't produced by traditional Zieglar-Natta catalysts or ordinary metallocene catalysts (Zhang *et al.,* 2007).

One of the most common methods to produce polyethylene is based on Ziegler-Natta catalysis. Alternatively, homogeneous Ziegler-Natta catalysis can be used which often incorporates metallocene catalysts that could in turn comprise a range of late transition metals. For example, it was shown that palladium and nickel-based catalysts showed significant promise to give a range of different polyethylenes. Moreover, it has since been proven that previously side-lined transition metal catalysts based on iron and cobalt have potential as successful polymerization catalysts. It is thought that the mechanisms for reactions such as these, and for reactions that will be explored in this paper, are as follows:

Activation and initiation

The activation mechanism of $LFeCl_2$ pre-catalyst by MAO is still under debate. Figure 1 shows the proposed species that the pre-catalyst form with the existence of MAO (Bianchini *et al.,* 2006).
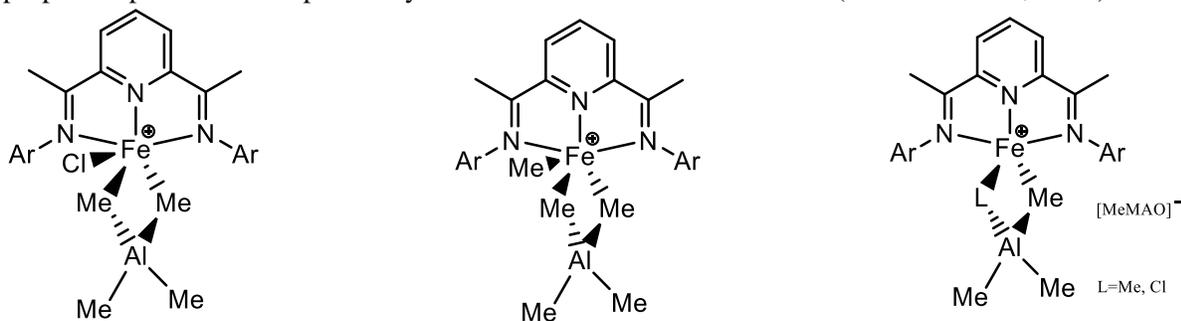
**Fig. 1: Proposed active Fe^{II} catalyst structure** (Bianchini *et al.,* 2006).

The mechanism that the ethylene attaches to the metal center is also unclear, but it is also proposed that the active metal center helps with the attachment so that to initiate the reaction as shown in figure 2.
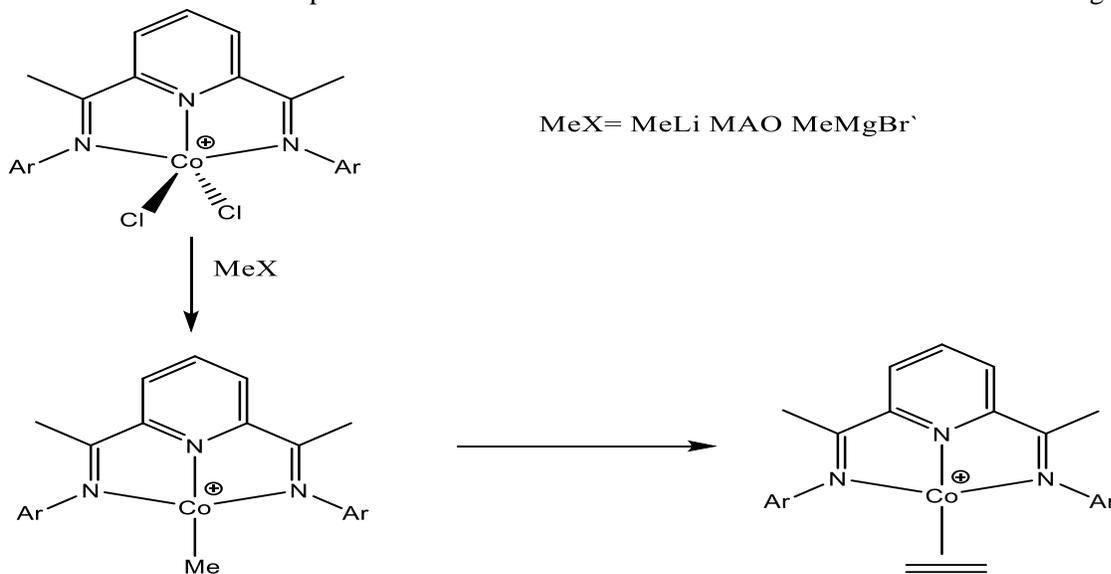
Fig. 2: Proposed initiation step for the catalyzed polymerization/oligomerisation (Bianchini *et al.,* 2006).
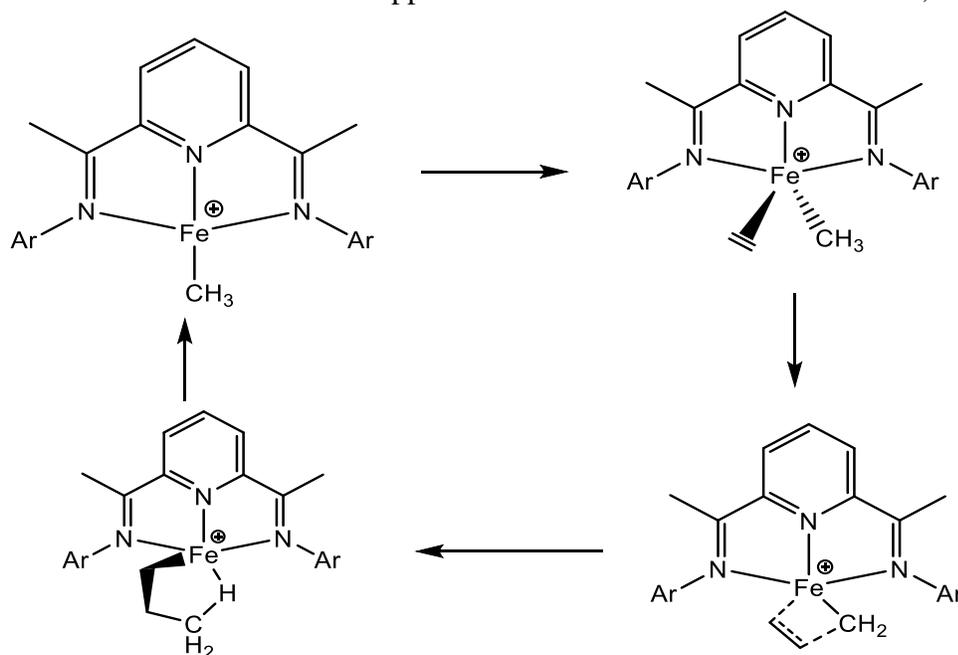
Propagation

When the metal center attaches a methyl group and the ethylene, the propagation is believed to follow Cossee-Arlman mechanism as shown in figure 3. Monomers keep on attaching to the metal center and insert into the chain.
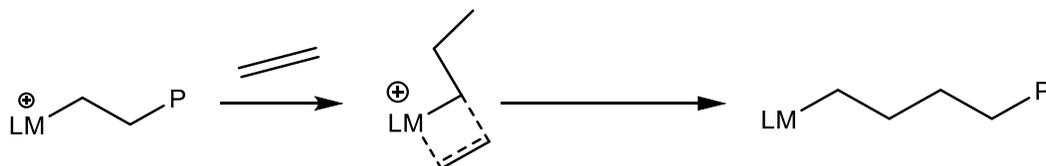
Fig. 3: Propagation via Cossee-Arlman mechanism (Bianchini *et al.,* 2006).

The insertion is assumed to happen via the four-centered transition state, is shown in figure 4.

Fig. 4: Propagation mechanism proposed by Gould and Gibson (Bianchini *et al.,* 2006).

Chain transfer and termination

The propagation steps keep on until chain transfer occurs. Macromolecules generate after the chain transfer, while the active metal center is ready for another chain. The mechanism for chain transfer is proposed in figure 5 (Bianchini *et al.,* 2006).

B-H transfer to metal

B-H transfer to monomer

chain transfer to aluminium
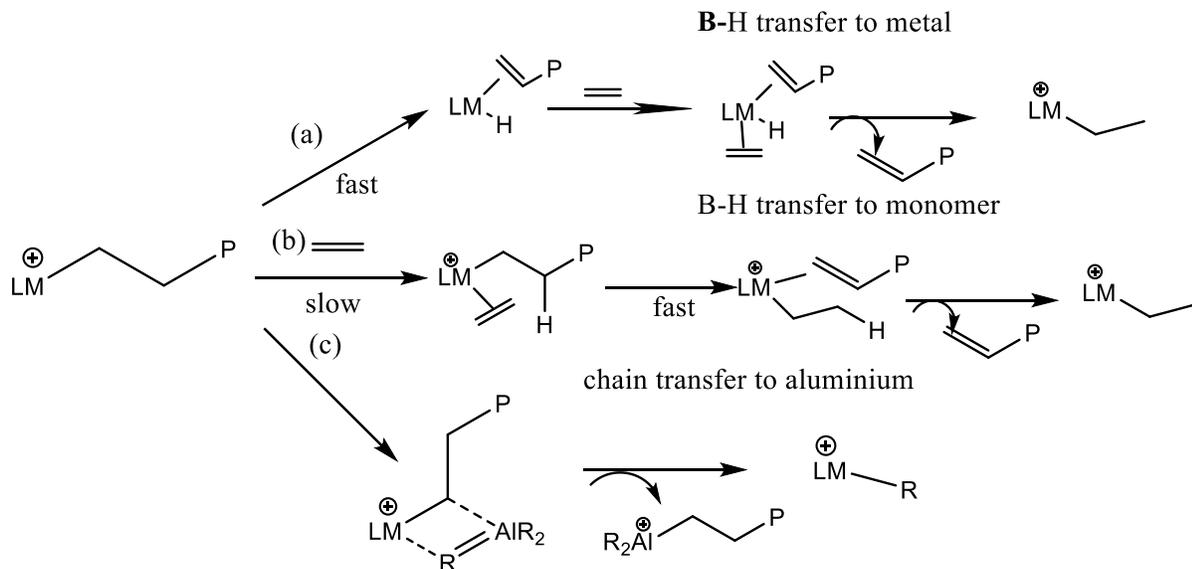
Fig. 5: Proposed chain transfer mechanisms in ethylene polymerization (Bianchini *et al.,* 2006).
This paper aims to explore a range of two distinct pre-catalysts, distinguishing whether they catalyze the formation of polymers, the yield to which the pre-catalyst can be produced and the yield at which the end product is also produced. It is our hope that meaningful comparisons can be made between the two pre-catalysts to determine which the most successful polymerization catalyst is.

2.   **Polymerization Experiment**

2.1 Synthesis of Ligand from 2,4,6-trimethylaniline

The ligand was prepared using 4.6 mmol of 2,4,6- trimethylaniline combined with of 2,6-diacetylpyridine (0.3 g, 1.84 mmol), few drops of glacial acetic acid was added. The reaction was carried out in a 25 mL round-bottomed flask (RBF). 5 mL ethanol was used as solvent. The solution was heated under refluxed for 20 hrs at $100^{\circ}C$. After which aliquots of the mixture was taken for mass spectroscopy and a H1 NMR analysis. Peaks were observed in the mass spectrum at 136, 281 and 398 Daltons, corresponding to the reactant, halfway product and final product respectively. The NMR data is given below:

NMR: H^1 (400mHz, 298K, $CDCl_3$): 2.0 (6H, s), 2.25 (6H, s), 2.3(6H, s), 2.80 (6H, s), 3.9 (10H, s) 6.91(4H, s), 7.91 (1H, t), 8.57 (2H, d)
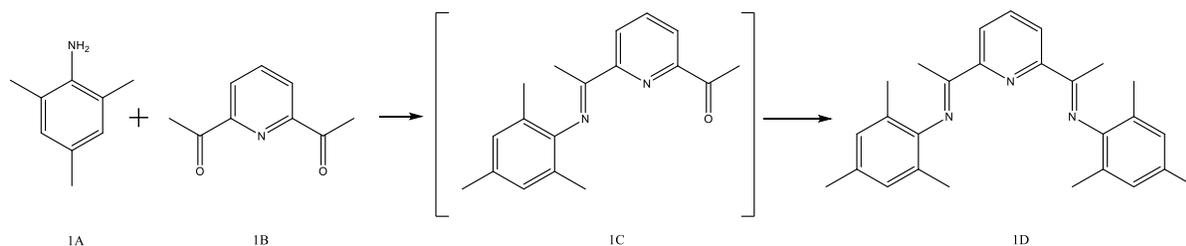
Fig. 6: Reaction scheme of the first reaction (2,4,6-trimethylaniline).
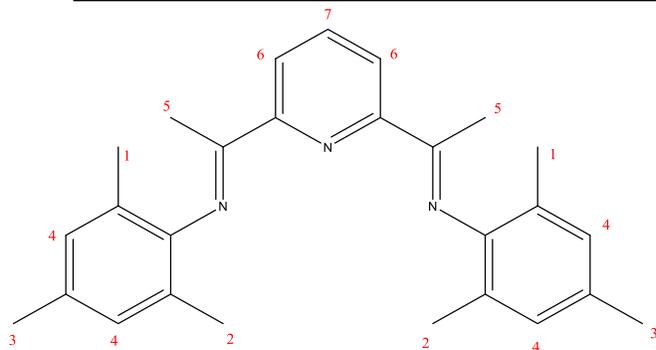
Fig. 7: Hydrogen environments of the ligand prepared from 2,4,6-trimethylaniline.

2.2 Complex synthesis (2,6-bis[1-(2,4,6-trimethylphenylimino) ethyl]pyridine)

After the first analysis, the remaining mixture in the flask was again heated under reflux for additional 48 hours. At the completion of this process, the reaction vessel was cooled by submerging in a dry ice/acetone bath before been filtered by vacuum filtration. The resulting solid pro duct was washed with cold ethanol. The yield of the product obtained was about 76.5% (0.731g) and it has a melting point of 106-110°C. The sample was then characterized by H^1 and ^{13}C NMR, IR spectroscopy and mass spectroscopy. The infrared spectrum presented a characteristic amide peak at 1636.26 cm^{-1}, while the mass spectrum recorded at this point showed most significantly a peak at 398 Daltons – corresponding to the $[M + H]^+$ion. The NMR data is given below:

NMR: H^1 (400mHz, 298K, CDCl$_3$): 2.07 (6H, s), 2.24 (6H, s), 2.37(6H, s), 2.79 (6H, s), 6.91(4H, s), 7.91 (1H, t), 8.57 (2H, d)

NMR: C^{13} (400mHz, 298K, CDCl$_3$): 16.41, 17.72, 17.87, 20.39, 20.74, 76.77, 77.02, 77.28, 122.21, 125.30, 128.57, 128.93, 132.24, 136.80, 146.20, 155.22, 167.47
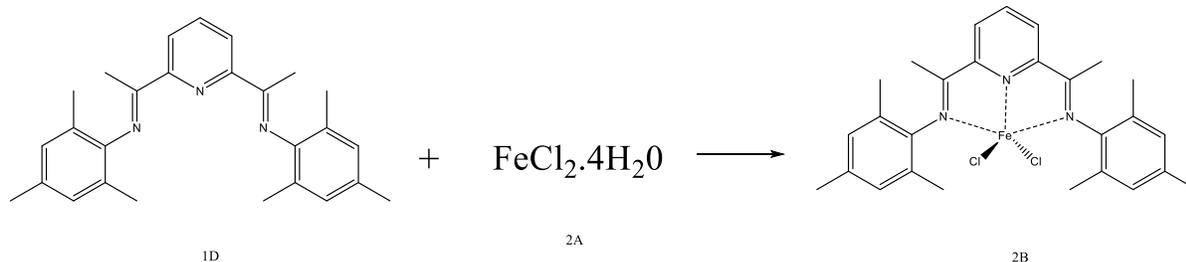
Fig. 8: Reaction scheme of the second reaction (2,4,6-trimethylaniline).

In the next step after getting the product (ligand), a 250 mL three-necked RBF was dried in an oven, then fitted with a nitrogen bubble, a young's tap and a rubber seal. After this setup the rubber seal was removed for the smallest time possible and 0.68 mmol FeCl$_2$.4H$_2$O and the previously prepared ligand (fig. 8) was added to the system. 10 mL of dry THF was added to act as solvent. The mixture was stirred for 1 hour and petroleum spirit was added to facilitate formation of a precipitate. After which the mixture was filtered using a Buchner funnel and transferred to a clean, dry, pre-weighed RBF. Due to the paramagnetic nature of the product NMR spectra were not recorded, however, an infrared spectrum was recorded which again showed the expected amide peak at 1620.89 cm^{-1}. In addition, a mass spectrum was recorded that showed peaks at 398, 453, 488.5 and 524 Daltons, each of which correspond to an expected fragment of the compound. To record an atomic absorption spectrum, a stock solution containing 100 mg/L iron was created using ammonium ferrous sulphate. From this, five calibration solutions ranging from 1 mg/L iron to 5 mg/L iron were created by dilution of the stock solution using deionised water. Samples were prepared from the pre-catalysts of the entire group calculated to have 3 mg/L iron content. It was determined the iron content was 3.45 mg/L, which can be explained by addition of too much compound while making the solution. Next, the effective magnetic moment of the pre-catalyst was

determined by use of an Evans balance. An empty Guoy tube was weighed and had its reading in the balance recorded, before being tightly packed with pre-catalyst up to 1.7 cm at which point both the mass and Evans reading were again recorded. Using this data, it was calculated using the below equations that the effective magnetic moment was 4.436, which fits the high spin Fe^{2+} component of the compound.

$$x_g = \frac{c \times l \times (R - R_O)}{1 \times 10^9 \times (m - m_0)}$$

$$x_m = RMM \times x_g$$

$$x_a = x_m + 2x_{Cl} + 3x_{pyridine}$$

$$\mu_{eff} = 2.828\sqrt{x_a T}$$

Where:
c= calibration constant, l= length of sample in tube, R=reading on Evans balance (full), R_0=reading on Evans balance (empty), m=mass of tube (full) and m_0=mass of tube (empty).

2.3 Polymerization of Ethylene from 2,4,6-trimethylaniline
All catalyst and polymerization procedures were carried out under dried N_2. Polymerization was carried out in a 250 mL round bottomed Schlenk flask. The polymerization was started by mixing 3.97 mg of the pre-catalyst with 40 mL of dry toluene. The mixture was stirred for 5 minutes and to the resulting solution 1.55 mL MAO was added via syringe, to start the ethylene polymerization causing a color change from blue to orange. The flask was evacuated and placed under 0.5 bar ethylene. After 30 minutes, 5 mL HCl was added, and the polymerization reaction was terminated. The solid polymer (polyethylene) was recovered by filtration, with a yield of 1.507 g and a melting point ranging from 105-110ºC. After filtration the polymer was washed with methanol and finally dried with magnesium sulphate and the solvent was recovered by rotary evaporator. Toluene (40 mL) was used as a solvent. MAO was used as the co-catalyst.

2.4 Synthesis of Ligand from 2,6-dimethylaniline
The NMR of the starting chemicals were determined in $CDCL_3$ and compared with standard NMR Spectra to ascertain their degree of purity before the reaction.
The ligand was synthesized using 4.60mmol of 2,6-dimethylaniline, a liquids. 0.6ml of 2,6-diacetylpyridine was added to a clean dried 25ml round bottom flask (RBF) with a stir bar. 5 ml of absolute ethanol and 0.60ml of 2,6-dimethylaniline was put into the RBF using micro syringes. Few drops of glacial acetic acid were added and yellow solution was then heated on a hotplate equipped with thermostat. The temperature of the hotplate and the thermostat were set at 110ºC and 100ºC respectively and left to reflux for two (2) nights.
After the first night the hotplate was put off and the reaction allowed cooling to room temperature to monitor the reaction. Small sample of the reaction were obtained and proton NMR and mass spectroscopy (MS) were run for the reaction. The NMR was in $CDCl_3$ while the blank for the mass spectroscopy was methanol.
The reaction was continued with the addition of micro pipettes of 2,6-dimethylaniline with 2 drops of glacial acetic acid. The reaction was left to continue for 48hours at the initial temperature of the reaction before its stoppage. The reaction was stopped after 48hours and the color of the solution was light brown. The solution was allowed to cool. The product was put into an ice bath with acetone and dried ice then left to crystallized. The yellow crystals were filtered under vacuum and the yellow crystal in the RBF washed using cooled ethanol and the filtrate further cooled in the ice bath containing dried ice with acetone. The yellow crystals were weighed and characterized using NMR, IR and MS.

2.5 Complex synthesis of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine
50ml 3 neck RBF was fitted with nitrogen bubbler, stir bar, cork and a source of nitrogen gas at 1 atmosphere. The RBF was made inert with a continuous supply of nitrogen. After 30minutes, 0.150g of the ligand and 0.080g of Iron (II) chloride tetrahydrate were put into the RBF with the aid of a bosh funnel. 10ml of dry Tetrahydrofuran (THF) was introduced into the RBF using a glass syringe. The reaction were stirred at 500 and at room temperature for 2hours and resulted in the formation of a deep blue solution. 10ml of n-hexane were added to the deep blue solution and filtered under vacuum and dried under pressure. The weight of the complex was determined. The complex was characterized with NMR, IR, MS, AAS and the Evans Balance.
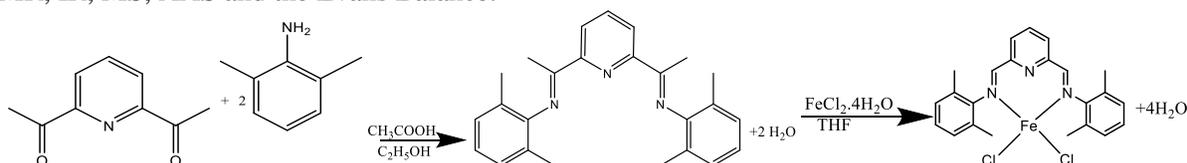
Fig. 9: Reaction scheme for the formation of ligand and pre-catalyst from 2,6-dimethylaniline.
2.6 Polymerization of ethylene from 2,6-dimethylaniline
A clean oven dried 250ml Schlenk flask was made inert by nitrogen gas supplied continuously for a period of the reaction. The flask was filled with 40ml of dried toluene and 0.0005g (0.01mmol) of the vacuum dried pre-catalysts was put into the flask and stirred magnetically for 5minutes. 1.50ml of MAO was syringed from a bottle previously bubbled with nitrogen gas for some minutes. Care was taken to ensure that the MAO doesn't touch the edges of the flask. An instant colour change was observed from deep blue to orange. Nitrogen gas was then exhaled from the flask completely as the valve was opened. Ethylene gas was then put into the flask as the contents were stirred magnetically at a pressure of 0.50 bar for the duration of the reaction. 30 minutes later the ethylene gas supply was stopped. The polymerization reaction was then terminated by the addition of 5ml hydrochloric acid. It produced a white polymer which was filtered under vacuum and all the contents in the flash were washed with toluene and the polymer vacuum dried, weighed, and characterized with the IR.

Mass of the ligand has noticeable peak at 121, 288 halfway products with sodium ion & 392 due to the ligand with the addition of sodium ion. MS for the complex was as follows, - 121, 267 halfway product ions, 424 less 2 atoms of chloride ions from the complex. The proton NMR of the half way product was 1H NMR (400MHZ, CDCl3) d2.2(S,12H), d2,8(S,6H),d6.9(d,1H), d7.2(d,1H), d7.9(d,1H), d8.5(d,1H). Titrate of the ligand proton and carbon NMR are as follows; 1H NMR (400MHZ, CDCl3) d2.2(S,12H), d2.90(S,6H), d6.91-7.1(d,2H), d7.90 (d,1H), d8.5(d,1H). While that for ^{13}C NMR (400MHZ, CDCl3) d 130,127,125,77,18,16.

3. RESULTS AND DISCUSSION
Table 1: Hydrogen environments and their corresponding shifts

Hydrogen environment	Chemical shift (ppm)
1	2.37
2	2.24
3	2.07
4	6.91
5	2.79
6	8.57
7	7.91

From the perspective of the ligand formed from 2,4,6-trimethylaniline was analyzed by means of multiple spectroscopic methods. Firstly, a H^1 NMR spectrum was acquired. Table 1 indicates which peak each hydrogen environment corresponds to. The absence of the halfway product 1C (fig. 6) was proven by the disappearance of a characteristic peak around 3.7 ppm corresponding to the methyl group adjacent to the

ketone observed by comparing two NMR spectrums, one taken halfway through the reaction and the other taken after the reaction was complete. Full characterization of compound 1D (fig. 1) was also accomplished by C^{13} NMR, IR spectroscopy and mass spectroscopy. IR spectroscopy provided additional evidence that the reaction had reached completion, the absence of a carbonyl peak around 1700 cm^{-1} proves the halfway product is not present in significant quantities, while the peak at 1636.26 cm^{-1} is characteristic of the amide stretching frequency. Mass spectroscopy further proved the product obtained was in fact compound 1D (fig. 6) as the most substantial peaks at 398 and 399 Daltons accurately correspond to the expected molecular ion and [M+H]$^{+}$ peaks, as well as the significant reduction of intensity regarding the peaks at 281 and 136 Daltons, seen in the mass spectrum taken halfway through the reaction. Sample was obtained with a reasonable yield of 76.5% and melted between 106 and 110°C.

Compound 2B (fig. 8) was characterized by IR spectroscopy, mass spectroscopy, determination of magnetic moment, atomic absorption spectroscopy and measurement of melting point. Infrared data showed that the amide stretching frequency at 1620.89 cm^{-1} was maintained, while no additional unexpected peaks appeared on the spectrum. Mass spectroscopy also presented acceptable results, predicted peaks at 398, 524, 453 and 488.5 Daltons were observed with varying intensities corresponding to L, $LFeCl_2$, LFe and $LFeCl^{+}$ fragments respectively, where L represents the ligand 1D. By use of Evans balance, μ_{eff} was calculated to be 4.436, fitting the proposed structure 2B (fig. 8) in which Fe^{2+} in a high spin configuration contains four unpaired electrons. Atomic absorption spectroscopy determined iron content in the sample was within reasonable to what was expected. Furthermore, the melting point was calculated to be in the range of 323-326°C, and the pre-catalyst 2B (fig. 8) was produced in a 79.7% yield. Finally, the polyethylene produced using this pre-catalyst was calculated to have a melting point range of 105-110°C, which is within the range quoted in the literature.

Table 2: Productivity of complexes

Complex	Polyethylene	Yield/g	Productivity/g mmol^{-1} hour^{-1} bar^{-1}
2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine	Polymer	14.36	5744
2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine	Polymer	1.507	602.8

Table 3: Yields obtained from the three steps.

Compound	Polymer/Oligomer	Yield 1	Yield 2	Yield 3
2,4,6	Polymer	0.731g/76.51%	0.284g/79.7%	1.507g
2,6	Polymer	0.260g/34.6%	0.290mg/143%	14.36g

Similarly, the ligand formed from 2,6-dimethylaniline, the mass of the ligand obtained from the initial reaction was 0.26g which corresponds to a yield of 35%. The weight of the iron complex produced was 0.29g which is a yield of 45%. For the polymerization reaction the weight of polyethylene obtained was 14.63g. Also, the mass of iron in the complex was determined to be 2.80 with the atomic absorption spectroscopy (AAS). The magnetic moment for iron was calculated as 4.40 from the data obtained from the Evans Balance equipment, (mass of sample tube = 1.46g, mass of sample= 0,03g, height of sample-1,50cm and reading of sample-268 and reading of the tube=-0.60) IR spectra for the ligand showed a C=N stretching attached to a methyl at 16.41.85 cm^{-1}and C=N stretching attached to pyridine at 1567.59 cm^{-1}.IR for iron complex shows a C=N stretching attached to a methyl at 1600.66 cm^{-1} and C=N stretching attached to pyridine at 1577.24.

IR spectra of the polymer shows polyethylene picks at 2915.01 cm^{-1} and 2847.53 cm^{-1}, and C-H stretching at 1472.05 cm^{-1} and 1462.36 cm^{-1}, C-C bond stretching at 816.23 cm^{-1} and 718.13cm^{-1}. The mass spectroscopy showed as noticeable peaks for the halfway reaction at 122, 164, 267, 370, ligand and the iron complex (pre-catalysts) and also the proton NMR of the ligand

CONCLUSION
It can be concluded from the study that the two analine derivatives used as catalysts produced good polymers and also the complex 2,6-bis[1-(2,4,6-trimethylphenylimino) ethyl]pyridine is a more productive pre-catalyst in the production of polyethene as compared to the complex 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine. From the results it also shows that 2,6-dimethylaniline has the largest amount of the polymer formed but there seems to be errors in the magnitude. So, we can conclude by saying 2,4,6-trimethylaniline is a better catalyst in the polymerization of ethylene formation.

REFERENCES

Bennett, A.M.A and Schiffino, R.S., (2000). Developing novel commercially viable catalysts for ethylene polymerization, Polym Prep Am Chem Soc Div Polym Chem, 41: 403-410.

Bianchini C, Giambastiani G, Rios I G, et al. (2006). Ethylene oligomerization, homopolymerization and copolymerization by iron and cobalt catalysts with 2, 6-(bis-organylimino) pyridyl ligands[J]. *Coordination chemistry reviews,* 250(11&12):1391-1418.

Hossein Z. G., Saman D., Saeid A., Reza, S., and Mohammad A. S., (2014). Synthesis of high molecular weight polyethylene using FI catalyst. *Polyolefins Journal,* 1(1): 25-32.

Nazeeha Alkayal (2016). Design, Synthesis and Characterization of Polyethylene-Based Macromolecular Architectures by Combining Polyhomologation with Powerful Linking Chemistry. King Abdullah University of Science and Technology Thuwal, Kingdom of Saudi Arabia, PhD Dissertation.

Schoeneberger, E. M. and Luinstra, G. A., (2021). Investigations on the ethylene polymerization with Bisarylimine pyridine Iron (BIP) catalyst. Catalysis, 11: 407.

Zhang H, Katao S, Nomura K, Huang J, (2007). Synthesis of half-titanocenes containing phenoxy-imine ligands and their use as catalysts for olefin polymerization. *Organometallics,* 26: 5967-5977.