ABSTRACT

High Performance Bulky α-Diimine Nickel(II) Catalysts for Ethylene Polymerization

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Bulky aryl α-diimine nickel(II) complexes with hydroxy functionality at the para-aryl position based on acenaphthenequinone with high efficiency were synthesized and characterized. These hydroxy functionalized ligands with different substitutes on their 2,6-ortho-aryl position including methyl, isopropyl, phenyl, 4-t-butyphenyl were used in ethylene polymerization. Ethylene polymerization was carried out using α-diimine nickel(II) complexes at different concentrations of ethyl aluminium sesquichloride (EASC) as an efficient cocatalyst. The effects of polymerization temperature from 10°C to 60°C and hydrogen concentration on catalysts performance were also investigated. The highest activity was achieved at 45°C and the activity was decreased at higher temperature for catalysts b and d the same as b'. The behaviours of these complexes were also compared with the same catalysts without hydroxy functionality. As expected, the α-diimine catalyst bis[N,N’-(4-(3-hydroxy-propyl)-2,6-di((4-t-butyphenyl)-phenyl))imino]acenaphthene nickel(II) dibromide (d) and bis[N,N’-2,6-di((4-t-butyphenyl)-phenyl)imino]acenaphthene (d’) had higher yield and molecular weight because of higher steric blocking of metal axial sites which leads to higher insertion rate of monomer and retardation of chain transfer. These catalysts polymerized ethylene in 45°C and 10 bar monomer pressure with exceptional activity up to 30.1×10^6 g PE/mol Ni.h. In the case of 2,6-di-(4-t-butyphenyl) aryl α-diimine nickel(II) catalysts, the molecular weight increased up to 3.9×10^6 g/mol with polydispersity index of 4.74. Despite the behaviour of Brookhart catalysts, this α-diimine catalyst d did not show any significant drop in its activity in presence of hydrogen which was added to polymerization reaction to control polymer molecular weight.

INTRODUCTION

The development of early and late transition metal catalysts for ethylene and propylene polymerizations has been the hot subject of recent studies in organometallic and polymer chemistry [1-4]. Although early transition metal catalysts dominate the commercial polymerization process, yet some shortages in these catalysts created a trend towards the development of late transition metal catalysts. Handling of early transition metal catalysts is difficult and monomers with functional groups act as poison for these catalysts due to their high Lewis acidity and oxophilicity of their active centres. In contrast to early transition metal catalysts, oxophilicity of late transition metal catalysts are lower and they are more tolerant towards polar
monomers [5-8]. These advantages have led to intensive research activities on late transition metal catalysts for polymerization of \( \alpha \)-olefins. Early late transition metal catalysts are hydrated to dimerize or oligomerize ethylene due to competing insertion and \( \beta \)-hydride elimination reactions [9-13]. Brookhart et al. have reported \( \alpha \)-diimine palladium and nickel(II) complexes that polymerize ethylene with high insertion reaction rates to produce polyethylene with high molecular weight with different types of branches along the polymer chains due to chain walking phenomena [4,11-15]. The microstructure of the produced polymer depends on ligand structure of \( \alpha \)-diimine complexes [16,17]. Brookhart et al. used 2,6-dimethyl or diisopropyl anilines to synthesize \( \alpha \)-diimine nickel(II) complexes. The steric demand of substituents on the aniline moieties and their orientation towards the virtual apical positions of the square-planar complexes is crucial for an optimal alignment of the incoming monomer relative to the growing polymer chain. Clearly, it is fundable that the steric effect of substituents blocks associative olefin exchange and it efficiently retards to chain transfers [18-21].

Consequently, \( \alpha \)-diimine catalysts of Brookhart polymerize ethylene and \( \alpha \)-olefins to high molecular weight polymers with activity comparable to early transition metal catalysts when nickel is used as active centres. One of the interesting differences between early transition metal and these catalysts is in microstructure and properties of their resulting polymers [10,18,19]. The microstructure of the obtained polymers using \( \alpha \)-diimine nickel(II) catalysts are greatly dependent on polymerization condition, ligand structure and metals used as active centres. For example, polyethylene produced by nickel(II) complexes can be highly branched and soft as elastomers or a linear rigid crystalline plastic, depending on polymerization condition and ligand structure [10].

Polymerization of ethylene using catalysts with hydrogen instead of bulky substituent in ortho-aryl positions leads to oligomerization of ethylene or \( \alpha \)-olefins, as bulky substituent in the ortho-aryl position increases insertion reaction rates in comparison with chain transfer reaction rates. Nevertheless, bulky substituted \( \alpha \)-diimine complexes are more stable than complexes without bulky substituted at higher polymerization temperature. This characterization creates an opportunity for bulky substituted \( \alpha \)-diimine complexes to polymerize ethylene to high molecular weight product [18-21]. As reported by Brookhart et al., the activity of 2,6-dimethyl and isopropyl \( \alpha \)-diimine nickel(II) catalysts are sufficiently high to compete with early transition metal catalysts in low polymerization temperature. Unfortunately, the performance of these catalysts and molecular weight of the product are decreased sharply by increasing polymerization temperature [10]. To overcome these disadvantages, Rieger et al. reported a series of new \( \alpha \)-diimine ligands and complexes bearing bulkier substituent than \( \alpha \)-diimine ligands of Brookhart [18,21]. They synthesized 2,6-diphenyl and 4-\( \tau \)-butyl anilines to be employed in the synthesis of \( \alpha \)-diimine ligands.

These new \( \alpha \)-diimine nickel(II) catalysts bearing very bulky aryl groups orientate perpendicular to the ligand coordination plane, provide steric bulk above and below the square plane of active centres to increase catalyst stability and retard chain transfer reaction in favour of chain growth towards high molecular weight polyethylene [16-19,22,23].

One of the major characteristics of late transition metal catalyst is chain walking which involves sequential \( \beta \)-hydride elimination and re-insertion reactions. It is shown by Rieger et al. and Brookhart et al. that steric bulk ligands in \( \alpha \)-diimine nickel(II) catalysts affect \( \beta \)-hydride elimination reaction rates and change the quality and quantity of chain branching in ethylene polymerization [10,18,21,24]. In this work we have synthesized Brookhart's and Rieger's diimine ligands with and without hydroxy functionality by an efficient procedure. The effects of hydroxy functionality and polymerization condition such as temperature and Al/Ni molar ratio and hydrogen concentration on catalyst performance are evaluated.

Herein we present a new efficient procedure to produce \( \alpha \)-diimine ligands with hydroxy functionality using a recoverable immobilized Pd catalyst. A series of diimine ligands and complexes bearing 2,6-disubstitution (alkyl or aryl) and 4-hydroxy functionality aniline moieties are synthesized. The steric and electronic effects of these substituents on
catalyst behaviour and the obtained polymers are simultaneously investigated. The most important perspective has been the synthesis of hydroxy functionalized steric bulky \( \alpha \)-diimine ligand with 4-\( t \)-butylphenyl substituents to improve catalyst activity in presence of hydrogen as well as its thermal stability.

**EXPERIMENTAL**

**Materials**

All solvents and reagents should be free of water and dissolved oxygen. Water content of methylene dichloride (CH\(_2\)Cl\(_2\)) and the other solvents like diethyl ether, hexane and toluene reduced to lower than 5 ppm by passing over molecular sieves (4 Å) or reaction with sodium wire followed by distillation. The nitrogen was dried by passing through the columns of molecular sieves 13XA with average pore diameter of 3-4 Å. All chemicals were added to the reaction vessels under nitrogen blanket. Syntheses of materials sensitive towards oxygen and water were carried out under dried nitrogen in dried glassware. Grace Davison silica was used without any treatment. The synthesized compound and sensitive material were manipulated in a nitrogen-filled glovebox at ambient temperature. Aniline, 2,6-diisopropylaniline, 2,6-dimethylaniline, sulphanilamide, 2-bromotoluene, 4-\( t \)-butylbenzyl, nickel bromide, acenaphthenquinone, lithium aluminium hydride, palladium acetate, tri-ethylamine, methyl acrylate, 10% palladium on activated carbon, bromine and acetic acid are purchased from Merck Chemical Co. (Germany). Anhydrous magnesium chloride was purchased from Aldrich Co. (USA) Hexane, hydrogen and polymerization grade ethylene were obtained from high density polyethylene unit of Bandar Imam Petrochemical Co. (Iran). 2,6-Dibromoaniline, tetrakis triphenyl phosphine palladium(0), c and d anilines and \( \alpha \)-diimine complexes, 4-bromo-\( t \)-butyl-benzol, benzoyl boronic acid, \( t \)-butylphenyl boronic acid, \( N \)-heterocyclic carbon palladium complex, ionic liquid matrix immobilized on silica and intermediate materials for a-d syntheses of \( \alpha \)-diimine complexes shown in Scheme I were synthesized according to the reported procedure [25-27].

**General Methods**

The synthesized compounds were characterized by \(^1\)H NMR analysis on a Bruker 500 and 300 MHz spectrometer (Germany) in CDCl\(_3\) and dimethyl-d\(_6\) sulfoxide. GC-Mass-QP5050A spectrometer from Shimadzu Co. (Japan) was used to characterize the
synthesized compounds. Ceramic dishes were used to sampling and dissolving of complexes for elemental analysis. Elemental analysis was done using an atomic absorption instrument (A-A-6800) from Shimadzu Co. Molecular weight and molecular weight distribution were measured by high temperature gel permeation chromatography by Research Department of Bandar Imam Petrochemical Co. in 1,2,4 tri-chlorobenzene at 140°C using a Waters GPC. Polystyrene standard was used to establish calibration curve. Melting point of the produced polymer was measured in a second heating run at a heating rate of 10°C/min using a differential scanning calorimetry (DSC-302) from BAHR Co. (Germany). Scanning electron microscopy (SEM) of supported catalyst and produced polyethylene was determined by a Philips XL-30ESEM (The Netherlands) equipped with an energy dispersive X-ray (EDX). Surface elemental analysis and the distribution of the elements Ni, Si, Mg and Al in catalyst particles were determined by an EDX. A Buchi reactor (500 mL and 1000 mL) was used for ethylene polymerization in slurry phase. This reactor was equipped by two thermal mass flow controllers and connected to the PC to record ethylene feed during polymerization.

**General Procedure for Bromination of Aniline Derivatives**

Before bromination reaction, the aniline group was chlorinated to increase the efficiency of this step. 2,6-Dialkyl or aryl aniline (1.0 equiv), dissolved in ether and hydrochloric acid (1.2 equiv), was added dropwise to the solution. The reaction was very fast and the hydrochloride of anilines was precipitated (white solid). After 30 min stirring at room temperature, the resulting mixture of white solid and ether was filtered and washed with cold diethyl ether (3×20 mL). The filtrate was dried and vacuumed at room temperature. The conversion of this reaction to desired product was between 95 to 97% (by weight) for different reacted anilines. In the second step, dried ammonium salt (1.0 equiv) was dissolved in acetic acid and methanol. Bromine (1.0 equiv) was added dropwise at room temperature to the solution. The mixture was stirred for 30 min. The brominated product was filtered and washed with ether and neutralized in ethereal solution by Na₂CO₃ solution (2 M).

**4-Bromo-t-butylbenzene**

Bromine (0.8 mol in 100 mL of glacial acetic acid), t-butylbenzene (1 mol), glacial acetic acid (50 mL), reduced iron powder (0.25 g), iodine crystals (0.25 g). Yield: 84%. ¹H NMR (300 MHz, CDCl₃/ TMS, 298 K): δ 1.32 (s, methyl, 9H), 7.28 (d, arom, 2H), 7.38 (d, arom, 2H).

**General Procedure for Boronic Acids Synthesis**

In a dried 250 mL Schlenk flask, 100 mL of diethyl ether and 1.02 equiv of crashed magnesium powder and a small piece of iodine crystal was added. The solution colour turned red. Some drops of aryl bromide were added to the flask. The solution colour went colourless, which was an indication of the start of the reaction. A condenser was connected onto the flask and the temperature increased to perform refluxing. Then, a solution of the aryl bromide (1 equiv) was added dropwise. Addition of aryl bromide was continued slowly and after complete addition, the reaction was continued for 30 min in reflux temperature. The prepared Grignard mixture was filtered and added dropwise and simultaneously with trimethylborate solution in diethyl ether into a jacketed 500 mL three-neck reactor and then filled with 100 mL dried diethyl ether under a very slow flow of dried nitrogen. The reaction temperature was kept under -70°C as it was very important to prevent reactions leading to products. Reagents were added to the reactor as rapidly as possible without the temperature of the mixture rising above -70±5°C. After complete addition, stirring of the mixture was continued and the temperature of reaction was allowed to reach 0°C. Then, hydrolysis of the mixture was carried out with 20 mL of distilled water during 5 min. The mixture was neutralized by sulphuric acid during 15 min. The organic layer was separated and aqueous layer was extracted by ether. The product was dried over MgSO₄ followed by evaporation of the remaining solvents. Then, the pure product was recrystallized in ethanol. The synthesis of boronic acids is shown in Scheme II.

**4-t-Butylboronic Acid**

1-Bromo-4-t-butylbenzene (120 mmol, 1 equiv), crushed magnesium (120 mmol, 1 equiv), trimethylborate (120 mmol, 1 equiv). Yield: 80%. ¹H NMR
(300 MHz, DMSO$_d$+CDCl$_3$/TMS, 298 K): δ 1.22 (s, methyl, 9H), 2.51 (s, OH, 2H), 7.35 (d, arom, 2H), 7.59 (d, arom, 2H).

**Phenylboronic Acid**

Bromobenzol (0.5 mol, 78.25 g), magnesium (0.5 mol, 12.32 g), trimethylborate (0.55 mol, 57.14 g), bright white solid. Yield: 92%. $^1$H NMR (300 MHz, DMSO$_d$+CDCl$_3$/TMS, 298 K): δ 2.11 (s, OH, 2H), 7.48 (3, arom, 3H), 7.78 (d, arom, 2H).

**General Procedure for Synthesis of Ortho-aryl-substituted Anilines from 2,6-Dibromoaniline by Suzuki Reactions**

2,6-Diaryl anilines were synthesized from 2,6-dibromoaniline. The amine group on phenyl ring increases the reactivity of ortho and para-positions. Therefore, 2,6-dibromoaniline was synthesized using sulphanilamide. The amine and sulphamide group activated ortho-position of sulphanilamide for bromination. Bromination was performed by hydrobromic acid addition to the solution of sulphanilamide. An initial heating was needed to start the reaction. The reaction was continued without heating and the heat of reaction increased the reaction temperature. The brominated product was precipitated, filtered and dried in a 70°C vacuum oven. The brominated compound was steam distillated in presence of sulphuric acid at 120°C. The product was purified in ethanol by crystallization and gave 78% yield.

Suzuki reaction procedure was used to C-C coupling and consequently 2,6-diaryl-substituted anilines syntheses (Scheme III) [22,23]. In a 250 mL Schlenk flask, fresh tetrakis(triphenyl phosphin)palladium [Pd(PPh$_3$)$_4$] (12 mol%) and 2,6-dibromoaniline (1 equiv) were dissolved in 100 mL of benzene and 6 equiv of Na$_2$CO$_3$ solution (2 M) was added. Then, a solution of arylboronic acid (2.2 equiv) in 50 mL ethanol while stirred and purged under nitrogen was added. The reaction temperature was increased to allow the reaction mixture to reflux for 72 h. The organic layer was separated and washed with water and the total aqueous phase was extracted with benzene. The solvent of organic phase was evaporated by heating under flow of dried nitrogen. The product as a wet cake was dispersed and dissolved in diethyl ether. Hydrochloric acid was added to the ethereal solution. Aniline was reacted with hydrochloric acid, and the produced ammonium hydrochloride was precipitated and filtered. The produced cake was washed with benzene until the obtained powder changed into white colour. This product was directly used for bromination but for production of α-diimine, it was necessary to neutralize the hydrohalogenated anilines to anilines. Subsequently the product was dispersed in diethyl ether and Na$_2$CO$_3$ solution was added dropwise to the mixture and it was stirred for 10 min. The organic phase was separated and the aqueous phase was extracted by diethyl ether. The solvent was removed by evaporation. The purity of product was determined by GC-Mass analysis before performing $^1$H NMR analysis.

**4-t-Butyl-terphenyl-amine**

In a 500 mL Schlenk flask, 2,6-dibromoaniline (15 mmol, 3.76 g), 4-t-butylboronic acid (45 mmol, 8.0 g), Pd(PPh$_3$)$_4$ catalyst (1.55 mmol, 1.8 g), 150 mL benzene and Na$_2$CO$_3$ solution (2 M, 90 mmol) were added. The whole mixture was refluxed for three days. Yield: 60%. $^1$H NMR (400 MHz, CDCl$_3$/TMS,
298 K): δ 1.35 (s, methyl, 18H), 5.05 (s, -NH₂, 2H), 7.00 (t, arom, 1H), 7.17 (d, arom, 2H), 7.47 (d, arom, 4H), 7.49 (d, arom, 4H).

2,6-Diphenylaniline
2,6-Dibromoaniline (36.0 mmol, 9.03 g), Pd(PPh₃)₄ (4.5 mmol, 5.82 g), phenylboronic acid (108 mmol, 13.2 g), Na₂CO₃ (216 mmol, 108 mL of 2 M solution). Reflux for three days. White solid crystal, Yield (7.5 g, 30.5 mmol): 85%. ¹H NMR (400 MHz, CDCl₃/TMS, 298 K): δ 4.55 (s, -NH₂, 2H), 6.95 (t, arom, 1H), 7.15 (d, arom, 2H), 7.35 (t, arom, 2H), 7.43 (t, arom, 4H), 7.51 (d, arom, 4H). GC-Mass (Rt = 23.5 min, purity>97% by weight).

General Procedure in Establishing Hydroxy Functionality on para-Position of 2,6-Dialkyl or Aryl Anilines by Heck Reaction
In the previous procedure, this reaction took place in presence of palladium acetate which was an expensive material and therefore a modified procedure was adopted for Heck reaction. In this procedure, the reaction between methyl acrylate and 2,6-disubstituted anilines is carried out in presence of a new N-heterocyclic carbon palladium complex and an ionic liquid matrix that is immobilized on silica. This catalyst system is recoverable and it can be used several times for the same Heck reaction. The catalyst was synthesized by a procedure reported by Karimi et al. [27] and immobilized on silica. The catalyst system [NHC-Pd/IL on silica], (0.01 mol% Pd, 0.02 g powder/1.0 equiv), dispersed in NMP and sodium acetate (0.5 equiv) was added to the mixture and stirred for 5 min. 4-Bromo-2,6-diaryl or alkyl aniline (1 equiv) and methyl acrylate (1.1 equiv) were added at room temperature and the reaction temperature was increased to 140°C and stirred overnight at this temperature. The resultant mixture was filtered and catalyst was separated and washed with (2× 20 mL) NMP, while the solution was washed with water. The water layer was extracted three times with diethyl ether and the organic layer was dried over anhydrous MgSO₄. The solvent was removed in vacuum oven at 70°C. The produced crude 3-(4-amino-3,5-dialkyl or aryl phenyl)-acrylic acid methyl ester was dissolved in THF and lithium aluminium hydride (2.5 equiv) was added slowly to the solution at 0°C. The temperature was increased to room temperature during 30 min after complete addition. The reaction was continued and the mixture was poured on the acidic ice. The organic layer was separated and aqueous layer was extracted three times with 50 mL diethyl ether. The organic portion was dried over MgSO₄. The mixture was filtered and solvent was removed. The GC-mass analysis showed its high purity, so the product was used directly for the next step. The hydrogenation of vinyl group in para-position of aniline was carried out under palladium catalyst on carbon active in acetic acid medium, by feeding of hydrogen flow through the solution for 24 h at room temperature. Hydrogenized aniline was separated by filtration from palladium catalyst. The
acetic acid was removed by evaporation under dried nitrogen flow.

3-(4-Amino-3,5-di(4-t-butylphenyl)phenyl)propan-1-ol

Step 1: brominated-4-t-butyl-terphenyl-amine was synthesized by 4-t-butyl-terphenyl-amine (3 g); methanol (20 mL), acetic acid (10 mL), diluted bromine (1.34 g) in 2 mL acetic acid, yield: 86%. GC-Mass (Rt = 18.15, purity higher than 95.5% by weight), 1H NMR (400 MHz, CDCl3/TMS, 298 K): δ 1.33 (s, methyl, 18H), 4.95 (s, -NH2, 2H), 7.28 (d, arom, 2H), 7.46 (d, arom, 4H), 7.48 (d, arom, 4H).

Step 2: 3-(4-amino-3,5-di(4-t-butylphenyl)phenyl)acrylic acid methyl ester was synthesized in a Schlenk flask, brominated-4-t-butyl-terphenyl-amine (3.5 g, 8.1 mmol), methyl acrylate (0.8 mL, 8.9 mmol), NaOAc (4.5 mmol), catalyst system [NHC-Pd/IL on silica], (0.01 mol% Pd, 0.03 g powder) in 20 mL NMP, yield: 75%. 1H NMR (400 MHz, CDCl3/TMS, 298 K): δ 1.42 (s, methyl, 18H), 3.80 (s, methoxy, 3H), 4.80 (s, -NH2, 2H), 6.28 (d, -CH=, 1H), 7.33 (d, arom, 2H), 7.47 (d, arom, 4H), 7.50 (d, arom, 4H), 7.67 (d, =CH-phenyl, 1H).

Step 3: 3-(4-amino-3,5-di(4-t-butylphenyl)phenyl)acrylic acid methyl ester (3.2 g), 100 mL THF, lithium aluminium hydride (1.2 g, 31.5 mmol) followed by hydrogenation in ethylacetate (20 mL), palladium (10% by weight) on activated carbon (30 mg, 0.027 mmol). Yield: 66%. 1H NMR (400 MHz, CDCl3/TMS, 298 K): δ 1.38 (s, methyl, 18H), 1.82 (pent, -CH2-, 2H), 2.2 (s, -OH, 1H), 3.77 (d, arom, 2H), 4.28 (d, -CH2-, 2H), 6.28 (triplet, -CH=, 1H), 6.65 (d, -CH=, 1H), 7.12 (triplet, arom, 2H), 7.25 (s, arom, 2H), 7.34 (triplet, arom, 4H), 7.51 (d, arom, 4H) followed by hydrogenation in ethylacetate (20 mL), palladium catalyst on activated carbon (30 mg, 0.027 mmol). Yield: 72%.

3-(4-Amino-3,5-diisopropyl-phenyl)-prop-2-en-1-ol

Step 1: 4-bromo-2,6-diisopropylaniline was synthesized by 2,6-diisopropyl aniline (100 mL, 530 mmol), water (400 mL), hydrochloric acid (100 mL), bromine (37.4 g, 234 mmol), methanol (100 mL), glacial acetic acid (50 mL). Yield: 88%. 1H NMR (300 MHz, CDCl3/TMS, 298 K): δ 1.28 (d, methyl, 6H), 2.95 (hept, -CH2-), 3.78 (s, -NH2, 2H), 7.18 (s, arom, 2H). Step 2: 3-(4-amino-3,5-diisopropylphenyl) acrylic acid methyl ester was synthesized by 4-bromo-2,6-diisopropyl aniline (17 mmol, 5.5 g), methyl acrylates (1.7 mL, 18.7 mmol), NaOAc (9.1 mmol), catalyst system [NHC-Pd/IL on silica], (0.01 mol% Pd, 0.063 g powder), 50 mL NMP. Yield: 87%. 1H NMR (400 MHz, CDCl3/TMS, 298 K): δ 3.76 (s, methoxy, 3H), 4.70 (s, -NH2, 2H), 6.28 (d, -CH=, 1H), 7.32 (s, arom, 2H), 7.47 (t, arom, 4H), 7.40 (d, arom, 4H), 7.66 (d, =CH-phenyl, 1H). GC-Mass (Rt = 16.89 min, purity>70% by weight).

Step 3: 3-(4-amino-3,5-diisopropylphenyl) acrylic acid methyl ester (14 mmol, 4.6 g), 100 mL dried THF, lithium aluminium hydride (35 mmol, 1.3 g). 1H NMR (400 MHz, CDCl3/TMS, 298 K): δ 3.76 (s, methoxy, 3H), 4.70 (s, -NH2, 2H), 6.28 (d, -CH=, 1H), 7.32 (s, arom, 2H), 7.47 (t, arom, 4H), 7.51 (d, arom, 3H), 7.40 (d, arom, 4H), 7.48 (d, arom, 4H).

3-(4-Amino-3,5-diisopropyl-phenyl)-prop-2-en-1-ol

Step 1: 4-bromo-2,6-diisopropylaniline was synthesized by 2,6-diisopropyl aniline (100 mL, 530 mmol), water (400 mL), hydrochloric acid (100 mL), bromine (37.4 g, 234 mmol), methanol (100 mL), glacial acetic acid (50 mL). Yield: 88%. 1H NMR (300 MHz, CDCl3/TMS, 298 K): δ 1.28 (d, methyl, 6H), 2.95 (hept, -CH2-), 3.78 (s, -NH2, 2H), 7.18 (s, arom, 2H). Step 2: 3-(4-amino-3,5-diisopropylphenyl) acrylic acid methyl ester was synthesized by 4-bromo-2,6-diisopropyl aniline (7.7 g, 30 mmol), methyl acrylates (3.0 mL, 33.0 mmol), NaOAc (15 mmol), catalyst system (NHC-Pd/IL on silica), (0.01 mol% Pd, 0.110 g powder), NMP (50 mL). Yield: 84%. 1H NMR (300 MHz, CDCl3/TMS, 298 K): δ 1.28 (d, methyl, 6H), 2.95 (hept, -CH2-), 3.78 (s, -O-CH3, 3H), 6.34 (d, -CH=, 1H), 7.25 (s, arom, 2H), 7.65 (d, =CH-phenol, 1H). Step 3: 3-(4-amino-3,5-diisopropylphenyl) acrylic acid methyl ester (26.8 mmol, 7 g), THF (150 mL), lithium aluminium hydride (67 mmol, 2.55 g). 1H NMR
3-(4-Amino-3,5-dimethyl-phenyl)-prop-2-en-1-ol

Step 1: 4-bromo-2,6-dimethyl-aniline (3a) was synthesized by 2,6-dimethylaniline hydrochloride (50 g, 317.5 mmol), bromine (50.5 g, 317.5 mmol), methanol (100 mL), glacial acetic acid (50 mL). Yield: 96%. 1H NMR (400 MHz, CDCl3/TMS, 298 K): δ 2.16 (s, methyl, 6H), 4.07 (s, -NH2, 2H), 7.06 (s, arom, 2H).

Step 2: 3-(4-amino-3,5-dimethyl-phenyl)-acrylic acid methyl ester synthesized by: 4-bromo-2,6-dimethyl aniline (6 g, 50 mmol), methyl acrylates (5.0 mL, 55.0 mmol), NaOAc (25 mmol), catalyst system (NHC-Pd/IL on silica) (0.01 mol% Pd, 0.185 g powder); NMP (50 ml). Yield: 83%. 1H NMR (400 MHz, CDCl3/TMS, 298 K): δ 2.17 (s, methyl, 6H), 3.78 (s, methoxy, 3H), 6.25 (d, -CH=, 1H), 7.14 (s, arom, 2H), 7.59 (d, =CH-phenyl, 1H).

Step 3: 3-(4-amino-3,5-dimethyl-phenyl)-acrylic acid methyl ester synthesized by: 4-bromo-2,6-dimethyl aniline (6 g, 50 mmol), methyl acrylates (5.0 mL, 55.0 mmol), NaOAc (25 mmol), catalyst system (NHC-Pd/IL on silica) (0.01 mol% Pd, 0.185 g powder); NMP (50 ml). Yield: 93%. 1H NMR (400 MHz, CDCl3/TMS, 298 K): δ 2.17 (s, methyl, 6H), 4.05 (s, -NH2, 2H), 7.06 (s, arom, 2H) followed by hydrogenation in ethylacetate (100 mL), palladium on activated carbon (0.09 mmol, 100 mg), flow of hydrogen. Yield: 80%. 1H NMR (400 MHz, CDCl3/TMS, 298K): δ 1.82 (pent, -CH2-, 2H), 2.17 (s, methyl, 6H), 2.55 (triple, -CH2=, 2H), 2.2 (s, -OH, 1H), 3.55 (triple, -CH2=, 2H), 3.95 (s, NH2, 2H), 6.52 (s, arom, 2H).

General Procedure for Synthesis of α-Diimine Ligands with Acenaphthenequinone Backbone and their Related Ni Catalysts

α-Diimine ligand was prepared by condensation reaction of acenaphthenequinone with the 2,6-dialkyl or allyl 4-hydroxy group substituted anilines. Anilines (2.2 equiv), acenaphthenequinone (1 equiv) and p-toluenesulfonic acid monohydrate (0.25 mol%) were dissolved in 75 mL benzene and condensation reaction was performed in a three-neck flask (100 mL) fitted with a Dean-Stark apparatus and a condenser under dried nitrogen atmosphere. The mixture was heated to reflux for three days and water by-product was constantly removed by water and benzene azeotrope. The solvent was removed under dried nitrogen and the product was purified by column chromatography (flash silica, ethyl acetate/hexane = 1:1). In the next step for α-diimine nickel(II) complex preparation, NiBr2(DME) (1 equiv) and α-diimine produced above (1 equiv) and 75 mL CH2Cl2 were added to a Schlenk tube and stirred at room temperature for one day. The resulted suspension was filtered and the solvent was removed under nitrogen flow and the resulted solid was washed with diethyl ether (3×20 mL) to give a solid catalyst.

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'- (2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']

Bis(N,N'-(4-(3-hydroxy-propyl)-2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and Bis(N,N'-(2,6-di[4-t-butyl-phenyl]-phenyl)iminofacenaphthene and their Nickel Complexes [d,d']
**Bis(N,N’-(4-(3-hydroxy-propyl)-2,6-di[(phenyl-phenyl)imino]acenaphthene and Bis(N,N’-(2,6-di[(phenyl-phenyl)imino]acenaphthene and their Nickel Complexes [c,c’]**

3-(4-Amino-3,5-diphenyl-phenyl)-propan-2-en-1-ol or 2,6-diphenylaniline (6 mmol),acenaphthene-quinone (0.5 g, 2.75 mmol), benzene (50 mL), p-toluenesulphonic acid monohydrate (0.25 mol%).

$^1$H NMR (400 MHz, CD$_2$Cl$_4$, 298 K): δ 1.77 (pent, -CH$_2$-, 4H), 2.74 (triple, -CH$_2$-, 4H), 3.35 (triple, -CH$_2$-, 4H), 3.46 (s, -OH, 2H), 7.44 (m, arom, 20H), 7.81 (m, arom, 6H), 8.32 (m, arom, 4H). The produced $\alpha$-diimine (0.752 or 0.636 g, 1 mmol), Ni(Br)$_2$(DME) (1 mmol, 0.31 g), CH$_2$Cl$_2$ (50 mL).

The catalysts c’ (0.82 g) and c (0.86 g) were produced in 96% and 89% yields, respectively. Elemental anal., calculated for C$_{54}$H$_{44}$Br$_2$N$_2$NiO$_2$: C, 66.76; H, 4.56; N, 2.88; Ni, 6.04; found: C, 66.52; H, 4.32; N, 2.92; Ni, 6.14. Elemental anal., calculated for C$_{48}$H$_{32}$Br$_2$N$_2$: C, 67.40; H, 3.77; N, 3.28; Ni, 6.86; found: C, 67.32; H, 3.62; N, 3.42; Ni, 6.75.

**General Procedure for Ethylene Polymerization**

Each batch of ethylene polymerization was carried out in a Buchi reactor equipped with magnetic stirrer and a thermal mass flow meter for measuring and recording feed streams and a thermocouple that connected to circulator to control reactor temperature. The reactor was heated and purged to remove poisonous elements for 2 h. The reactor was then cooled to room temperature and dried hexane (750 mL) was charged to the reactor under nitrogen atmosphere. A desired amount of diluted co-catalyst (ethyl aluminium sesquichloride) in hexane was added into the reactor by a syringe. Reactor stirrer was turned on for five minutes while all lines to reactor were close. The catalyst was weighed and dissolved in CH$_2$Cl$_2$. The solution was injected into the reactor by syringe while the stirrer was turned on. The speed of stirring was adjusted to 400 RPM and the reactor was pressurized by a desired amount of hydrogen (if necessary). Then, the reactor pressure was increased by continuous ethylene charging through the pressure regulator on ethylene cylinder. The reactor temperature was increased and controlled by a circulator at a desired temperature. After 1 h, the reactor was cooled and the reactor pressure was vented. The polymerization was terminated by injection of a 2% HCl/methanol solution into the reactor. The polymer solution or slurry was dried in vacuum oven at 70°C.

**RESULTS AND DISCUSSION**

**Ligand Synthesis**

Brookhart ligands [10] were synthesized by 2,6-diisopropyl aniline and 2,6-dimethyl aniline that are commercially available. 2,6-Diphenyl and 2,6-di(4-t-butyl phenyl) anilines were synthesized by palladium-catalyzed cross-coupling of aryl boronic acids with aryl bromides. Aryl boronic acids were also synthesized by reaction of aryl Grignard agents with trimethylborate. Finally, $\alpha$-diimine nickel(II) catalysts were synthesized in a simple reaction condition with high yields.

Bromination of 2,6-dimethyl, isopropyl, phenyl and t-butylphenyl anilines were carried out by adding Br$_2$ to a stirred solution of chlorinated anilines in glacial acetic acid. Phenyl and t-butylphenyl anilines were synthesized by Suzuki reaction between 2,6-dibromoaniline and Grignard reagent. 2,6-Dibromoaniline with a good yield was obtained via the bromination of acetalamide with bromic acid and followed by steam distillation. The crude anilines were synthesized via the modified Suzuki reaction in one pot [21,25]. These products were purified by precipitation with reaction of hydrochloride or bromide and produced bulky anilines in their ethereal solution (Schemes II and III).

The hydrochlorinated or brominated anilines were brominated directly with good yield by adding Br$_2$ to a stirred solution of chlorinated anilines in glacial acetic acid. Phenyl and t-butylphenyl anilines were synthesized by Suzuki reaction between 2,6-dibromoaniline and Grignard reagent. 2,6-Dibromoaniline with a good yield was obtained via the bromination of acetalamide with bromic acid and followed by steam distillation. The crude anilines were synthesized via the modified Suzuki reaction in one pot [21,25]. These products were purified by precipitation with reaction of hydrochloride or bromide and produced bulky anilines in their ethereal solution (Schemes II and III).

The hydrochlorinated or brominated anilines were brominated directly with good yield by adding Br$_2$ to the slurry of halogenated aniline in glacial acetic acid. In this study, mixture of methanol/glacial acetic acid as a reaction medium was used because of low solubility of ammonium salt in glacial acetic acid. Aqueous Na$_2$CO$_3$ (2 M) solution was added to neutralize the salted 4-bromoanilines and then, the product was extracted by diethyl ether. Palladium catalyzed Heck coupling reaction between the brominated aniline and methyl acrylate was applied to introduce hydroxy functionality in para-position of aniline. The methyl acrylate in para-position of anilines was reduced by lithium aluminium hydride.
followed by catalytic hydrogenation of vinyl group by palladium on carbon active (Scheme IV).

Consequently, the α-diimine nickel(II) catalysts with hydroxy functionality were synthesized in two steps: in the first step, α-diimine ligands were synthesized by reaction of 2,6-disubstituted anilines (a-d) and acenaphthenequinone and in the second step, the produced α-diimines ligands were reacted with

Scheme IV. Synthetic scheme of anilines with hydroxy functionality in para-position.
(NiBr₂(DME)) in dichloromethane (Scheme V).

Elemental analysis of α-diimine complexes confirmed the predicted chemical composition of all synthesized homogeneous catalysts. These compounds were air stable during handling and characterization.

**Ethylene Polymerization**

The results of ethylene polymerization experiments are shown in Tables 1 and 2. Catalyst performance of 2,6-diisopropyl substituted α-diimine nickel(II) complexes with and without hydroxy functionality at 10 bar ethylene pressure and different polymerization conditions such as temperature, hydrogen pressure, Al/Ni molar ratio and catalyst concentration are shown in Table 1. The results of polymerization runs with different ligand structures and the effect of polymerization temperature, Al/Ni molar ratio and hydrogen concentration on the performance of 2,6-di(4-t-butylphenyl) substituted α-diimine nickel(II) complexes are also summarized in Table 2.

As observed in the data in Table 1, the catalyst activity of b is higher than b' under the same condition (227 kg PE/g Ni versus 148 kg PE/g Ni). The similar results obtained for catalysts are: a and a' (152 kg PE/g Ni versus 98 kg PE/g Ni), c and c' (86 kg PE/g Ni versus 75 kg PE/g Ni) and d and d' (513 kg PE/g Ni versus 450 kg PE/g Ni). The data show that the presence of hydroxy functionality on para-position of aryl in α-diimines increases the activity of the catalysts. The results showed that the effect of hydroxy functionality in para-position of aryl on catalyst activity and molecular weight of the produced polymer is as high as the effect of substituent's in ortho-position of aryl (activity of b/activity of b' = 227/148 = 1.53 versus activity of b'/activity of a' = 73.8/48.8 = 1.51).

In Brookhart α-diimine catalysts, it is observed that ortho-substituents on the aryl rings of imine impose electronic and steric effects on the axial sites. The steric bulk substituent decreases the rate of chain transfer relative to the rate of propagation so

<table>
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<th>Precatalyst</th>
<th>Ni (μmol)</th>
<th>Temperature (°C)</th>
<th>Al/Ni</th>
<th>H₂ (bar)</th>
<th>Yield (g)</th>
<th>Productivity (kg PE/g Ni)</th>
<th>Mw×1000 (g/mol)</th>
<th>PDI (Mw/Mn)</th>
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Polymerization conditions: α-diimine nickel(II) catalysts, co-catalyst: EASC, solvent: hexane, ethylene pressure: 10 bar, time: 60 min, molecular weight and polydispersity were determined by GPC. Melting temperature was determined by DSC.
molecular weights of the produced polymers by these catalysts were increased significantly. In addition, the para-substituents have no significant steric effect on axial sites and this effect is relatively stronger on their electronic properties. A group in para-position that has electron withdrawing nature can increase electrophilic properties of nickel centres and increase their activity [22,23,28,29]. With this explanation, it was expected to observe a significant increase in the activity of catalysts containing hydroxy functionality on aryl rings' para-position.

In α-diimine nickel(II) the complexes with hydroxy functionality, the insertion reaction rates are higher than their chain transfer reaction rates and consequently the molecular weight of the polymer products increase due to the electron effect of this functional group [16,22,23,28,29].

The behaviour of catalysts b and b’ was similar in different temperatures and Al/Ni molar rates and hydrogen concentration. Ethylene polymerization using catalysts b and b’ were carried out at different temperatures from 10 to 60°C. At temperature higher than 60°C the catalyst decomposition and lowering solubility of ethylene are occurred and significant decrease in catalyst activity is observed. The effect of temperature on catalyst activity may be explained by Brookhart theory on deactivation mechanism of α-diimine catalysts [10]. The motion and rotation of aryl ring is increased at higher polymerization temperature. Therefore, coordination sites of the metal centre cannot coordinate with monomer due to C-H bond activation of an ortho alkyl substituent and activity of active centres are reduced sharply. In both catalysts b and b’, the activity is decreased sharply when the temperature increases from 45°C to 60°C, but an increase in catalyst activity is observed for both catalysts when the temperature is increased from 30 to 45°C that has been missed by Brookhart et al. on α-diimine nickel(II) catalyst b’ because they have selected their polymerization temperature with longer interval. This behaviour can be explained by a competition between higher reaction rate of active centres and deactivation rate that leads to maximum productivity at a specific temperature [10,18]. It is observed that hydroxy functionality increases the thermal stability of catalysts. For example, when the polymerization temperature is increased from 45 to 60°C, the activity of catalyst b’ is decreased from 148
to 85 kg PE/g Ni, whereas it is decreased from 227 to 147 kg PE/g Ni for catalyst b. The obtained data from ethylene polymerization in different Al/Ni molar ratios, from 250 to 1000, show that this activator is an efficient activator [30]. Aluminium alkyl co-catalysts activate active centres of late transition metal catalysts to form cationic nickel species for initiation of ethylene polymerization [15]. It is observed that increase of Al/Ni molar ratio leads to a slight drop of activity. This behaviour is also observed for catalyst d. As shown in Tables 1 and 2, the produced polymer has narrow molecular weight distribution and the molecular weight of polyethylene decreases with the increase of Al/Ni ratio. Aluminium alkyls act like chain transfer reagents in ethylene polymerization and chain transfer rate would be increased with Al/Ni ratio increasing and thus molecular weight of polyethylene is reduced. The performance of catalysts b and b' was dramatic when hydrogen added to polymerization reaction to control the molecular weight of the resulting polymers. This is one major drawback for commercialization of Brookhart catalysts in the presence of hydrogen for molecular weight control in industrial processes.

The chain transfer reaction rates are increased in presence of hydrogen that competes with monomer to coordinate with coordination sites of active centres. The catalyst activity and molecular weight of the produced polyethylene by catalysts b and b' are declined sharply in presence of hydrogen and this reduction is more significant at higher temperature. The main reason for reduced molecular weights at higher temperature is an increase in the rate of chain transfer, although degradation of catalyst can also affect the molecular weights.

The results in Table 2 show that the magnitude of steric bulk of ortho-substituents has a strong effect on catalysts activity and insertion reaction rates. It has been shown that the activity order of studied α-dimine nickel(II) catalysts is: d or d' > c or c' > b or b' > a or a'. The fact is that bulkier substituents increase insertion reaction rates of monomer to the active centres [10,18,21]. The orientation and strict position of phenyl groups in catalysts c, c', d and d' are found on points towards each other above and below the N-Ni-N plane [18,21]. This position and state of phenyl groups create steric bulk enough to increase insertion reaction rates. In contrast, the introduction of 4-t-butyl substituents on para-positions or ortho-positions of aryl rings leads to more repulsive interaction and increase steric bulk effect. The obtained data in Table 2 confirm this explanation and the catalysts d and d' have the highest strict bulk among others so their activities are at highest values. As expected, the molecular weight of a polymer with catalysts a to d and a' to d' is narrow and polydispersity index of the polymers is mostly between 1.5 to 3.0. The $T_m$ and physical appearance of produced polymer using the studied catalysts a to d and a' to d' were evaluated by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), respectively. The ligands structure and polymerization condition have strong influence on thermal behaviour and physical appearance of the polymers obtained [10].

Characterization of the polymers by differential scanning calorimetry (DSC) showed that the structure of the polymers with these catalysts is strongly dependent on ligand structure of the catalyst employed and polymerization temperature. For example, the DSC cure of the polymers using catalyst b showed broad melt transitions temperature ($T_m$’s) especially at higher temperature whereas it is narrow for linear various polyethylenes (Figure 1). In contrast, the shape of DSC curves represents a degree of linearity and some branching of the polymers obtained but, it is difficult to make a precise relationship between each branching number and reported $T_m$. It is suggested that the polyethylene produced in our experiment by catalysts b' and b are branched...
polyethylene. The larger the branching number leads to lower $T_m$ of the produced polyethylene with broader melting peaks. The melting behaviour of polyethylene is mainly related to the short chain branching density (SCBD) and its increase also leads to smaller lamellar thickness of crystal structure and consequently lower $T_m$ of the polymer [31,32]. Physical appearance of a polymer obtained by catalysts a and a’ is like a wax at high polymerization temperature and a white powder at low polymerization temperature. A flexible polymer is produced by catalysts b and b’ at 60°C whereas a white solid polymer is produced by catalysts d and d’. As it is reported by Rieger et al. [21], the microstructure of the polymers produced by catalyst d’ is linear so we have expected to produce linear polymer using catalyst d with melting temperature around 130°C.

The SEM images in Figure 2 show an irregular shape of polymer particles with low bulk density using catalysts d’ and d. It is shown that polymer morphology is not sufficient for polymer processing and it has motivated researchers to attach these catalysts specially d and d’ by covalent bonds onto supports to produce polymer particles with desirable morphology.

**CONCLUSION**

In this article, a series of steric bulky $\alpha$-diimine nickel(II) catalysts bearing hydroxy functionality were successfully synthesized. The effects of steric bulk substituents and hydroxy functionality were evaluated on catalyst performance in different polymerization conditions such as temperature, Al/Ni molar ratio and hydrogen concentration simultaneously. In evaluation of the effect of polymerization temperature, it was observed that catalysts b, b’ and d showed the maximum productivity at 45°C whereas this behaviour has been missed by other authors. In contrast, it is observed that hydroxy functionality increases thermal stability of the catalysts and lowers catalyst deactivation when temperature is increased from 45 to 60°C. Increase in Al/Ni ratio has led to slight drop in catalyst activity in comparison with the temperature effect and significant reduction in molecular weight of different polyethylenes obtained by catalysts b, b’ and d. The hydroxy functionality on para-position of ligands has led to significant increase in the activity of catalysts with methyl and isopropyl substituents, whereas the effect of hydroxy functionality has been weaker on activity of catalysts with steric bulky substituents. The application of hydrogen to tune molecular weight of polymer has led to significant reduction in activity of the catalysts a and b, and it has been less in case of catalyst d. The SEM images of the polymers showed irregular morphology and agglomeration of the polymers on reactor wall and agitator.

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