

Synthesis, Characterization, and Catalytic Ethylene Oligomerization of Pyridine-imine Palladium Complexes

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Abstract Two neutral five-membered pyridine-imine palladium complexes with the bulky dibenzhydryl ($\text{CH}(\text{Ph})_2$) substituted aniline were synthesized and fully characterized by nuclear magnetic resonance (NMR) and X-ray crystal diffraction. Well-defined cationic palladium complexes were further obtained by treatment of chloromethylpalladium complexes with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBArF) in CH_3CN . Cationic palladium complexes were capable of catalyzing ethylene oligomerization without any cocatalysts. The influences of catalyst structure, reaction temperature, and ethylene pressure on ethylene oligomerization were studied in detail. The introduction of bulky benzhydryl ($\text{CH}(\text{Ph})_2$) on the *ortho* position of the aniline moiety enhanced catalytic activity, thermal stability of the catalyst, and molecular weight of the obtained products. Highly branched oligomers with molecular weights of 600–800 g/mol and narrow polydispersities (1.03–1.12) were produced.

Keywords Palladium; Ethylene; Oligomerization; Branching

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INTRODUCTION

Great progress has been made in the area of late transition metal complexes as precursor catalysts for olefin polymerization over the last two decades^[1–9]. Among these late transition metal complexes, $[N,N]$ bidentate nickel and palladium complexes have received much attention because their catalytic activity and selectivity can be regulated through facile ligand modification^[10–14]. Particularly, α -diimine nickel and palladium complexes not only can precisely control polymer branching structure by chain walking process, but also prepare high-value polyolefins by the copolymerization of olefins and polar monomers because of their low oxophilicity^[15–32]. Tremendous amounts of efforts have been devoted to design and synthesis of α -diimine nickel and palladium catalysts for the homo- and copolymerization of ethylene with various polar monomer^[33, 34].

Besides α -diimine ligand, another important $[N,N]$ bidentate ligand is pyridine-imine, which can be regarded as an unsymmetrical α -diimine ligand. Pyridine-imine nickel and palladium catalysts usually catalyze ethylene polymerization with high activity, while produce oligomers or low-molecular-weight branched polyethylene (PE)^[35–39]. Because of less axially steric of the pyridine moiety, most investigations were focused on modification of *ortho*

substituents of aniline moiety and the bridging carbon of the pyridine-imine^[40]. Sun reported a series of pyridine-imine nickel complexes with different substituents on the *ortho* position of aniline, which afforded a mixture of α -olefins and low-molecular-weight PE^[41]. Laine designed and synthesized a series of dimeric pyridine-imine nickel complexes with different substituents on the bridging carbon, generating low-molecular-weight PE with $M_n < 20$ kg/mol above 0 °C^[42]. Chen reported that pyridine-imine nickel complexes containing both the dibenzhydryl and the naphthyl moieties polymerized ethylene with high activity and high thermal stability, producing PE with a molecular weight up to 1000 kg/mol^[43].

Compared with nickel based catalysts, pyridine-imine palladium catalysts are rarely studied and reported for ethylene polymerization because of low activity and poor thermal stability^[40]. Recently, dibenzhydryl substituted aniline was successfully used in modification of $[N,N]$ bidentate nickel and palladium complexes for olefin polymerization^[44–48]. The introduction of bulky benzhydryl group enhanced the catalytic activity, thermal stability, and the polymer molecular weight. Long reported that α -diimine nickel complexes with bulky dibenzhydryl anilines polymerized ethylene with high activity of $>10^6$ gPE/(molNi·h) at 100 °C, generating high-molecular-weight PE ($M_n = 564$ kg/mol) with controllable fashion ($\text{PDI} = 1.09\text{--}1.46$)^[49]. Chen designed and synthesized a series of α -diimine palladium catalysts with dibenzhydryl anilines, which showed the high activity and

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thermal stability, and produced high-molecular-weight PE with low branching degree^[50]. Compared with the analogues of isopropyl on the *ortho* position of aniline, obvious increase in activity and polymer molecular weight in ethylene polymerization was observed for the dibenzhydryl substituted pyridine-imine nickel complexes^[41, 51]. In this paper, two new well-defined pyridine-imine palladium complexes with dibenzhydryl substituted anilines were synthesized and characterized for ethylene oligomerization. The introduction of bulky dibenzhydryl group enhanced the catalytic activity and thermal stability of pyridine-imine palladium catalysts, and highly branched oligomers with narrow polydispersities (1.03–1.12) were produced.

EXPERIMENTAL

General Procedures

All manipulations involving air- and moisture sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard vacuum-line, Schlenk, or glovebox techniques.

Materials

Dichloromethane was distilled from CaH₂ under nitrogen, and toluene and hexane were from Na/K alloy. Acetonitrile was purchased from Aldrich Chemical and was distilled under reduced pressure before use. 4-Methylaniline, zinc chloride, benzhydryl, pyridine-2-aldehyde, 2-acetylpyridine, *p*-toluenesulfonic acid, 1,5-cyclooctadiene and tetramethyltin were purchased from Energy Chemical and used as received. Palladium chloride was purchased from HWRK Chem. Ethylene (99.99%) was purified by passing through Agilent moisture and oxygen traps. Other commercially available reagents were purchased and used without purification.

Synthesis of 2,6-Bis(diphenylmethyl)-4-methylaniline

2,6-Bis(diphenylmethyl)-4-methylaniline was prepared according to literature methods^[49, 51]. The product was obtained as a white powder in 75% yield. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 7.29–6.08 (m, 20H, Ph), 6.37 (s, 2H, Ar-H), 5.45 (s, 2H, CH), 3.27 (s, 2H, NH₂), 2.02 (s, 3H, CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 143.10, 139.97, 129.87, 129.58, 129.38, 128.80, 126.91, 52.73, 21.34.

Synthesis of [Pyridine-2-C(Me)=N-Ar] (L1) [Ar = 2,6-bis(diphenylmethyl)-4-methyl]

A mixture of 2-acetylpyridine (0.605 g, 5.0 mmol), 2,6-bis(diphenylmethyl)-4-methylaniline (2.19 g, 5.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid in toluene (80 mL) were refluxed for 6 h. After solvent evaporation at reduced pressure, the crude product was purified by recrystallization from ethanol as yellow crystal in 81% yield. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 8.58 (d, 1H, Py), 8.03 (d, 1H, Py), 7.71 (t, 1H, Py), 7.32 (t, 1H, Py), 7.28–7.00 (m, 12H, Ph), 7.01 (t, 8H, Ph), 6.68 (s, 2H, Ar-H), 5.26 (s, 2H, CH), 2.17 (s, 3H, CH₃), 1.06 (s, 3H, CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 169.81, 156.30, 148.76, 146.39, 144.05, 142.86, 136.36, 132.49, 131.82, 130.12, 129.75, 128.92, 128.58, 128.29, 126.50, 126.26, 124.88, 121.60, 52.35, 21.63, 17.17.

Synthesis of [Pyridine-2-CH=N-Ar] (L2) [Ar = 2,6-bis(diphenylmethyl)-4-methyl]

In a manner similar to that described for L1, L2 was prepared as yellow crystal in 68% yield. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 8.58 (d, 1H, Py), 7.68 (t, 1H, Py), 7.58 (d, 1H, Py), 7.28 (t, 1H, Py), 7.19–7.08 (m, 13H, Ph), 7.00 (8H, d, Ph), 6.64 (s, 2H, Ar-H), 5.44 (s, 2H, CH), 2.15 (s, 3H, CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 165.43, 153.92, 149.84, 148.35, 144.03, 143.10, 139.98, 136.62, 133.38, 132.79, 130.00, 129.87, 129.57, 129.37, 129.03, 128.80, 128.45, 128.19, 126.91, 126.46, 125.33, 122.46, 52.04, 21.53.

Synthesis of [Pyridine-2-C(Me)=N-Ar]PdMeCl (C1) [Ar = 2,6-bis(diphenylmethyl)-4-methyl]

The neutral pyridine-imine palladium complex C1 was synthesized by the reaction of (COD)PdMeCl with the corresponding pyridine-imine ligand L1 in dichloromethane. A typical synthetic procedure for C1 was described as follows: 1.2 mmol of ligand L1 and 1.0 mmol of (COD)PdMeCl were added to a Schlenk tube together with 20 mL of dichloromethane, and the reaction mixture was then stirred for 12 h at room temperature. The solution was evaporated under vacuum to 5 mL, and then 30 mL of hexane was added. Complex C1 was obtained as yellow powder in 69% yield. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): *trans*-isomer: 8.84 (d, 1H, Py), 7.96 (t, 1H, Py), 7.71 (d, 1H, Py), 7.25–7.01 (m, 20H, Ph), 6.97 (d, 1H, Py), 6.67 (s, 2H, Ar-H), 6.02 (s, 2H, CH), 2.16 (s, 3H, CH₃), 1.22 (s, 3H, CH₃), –0.15 (s, 3H, Pd-CH₃); *cis*-isomer: 9.36 (d, 1H, Py), 7.89 (t, 1H, Py), 7.71 (d, 1H, Py), 7.25–7.01 (m, 20H, Ph), 6.97 (d, 1H, Py), 6.81 (s, 2H, Ar-H), 5.94 (s, 2H, CH), 2.22 (s, 3H, CH₃), 0.97 (s, 3H, CH₃), –0.16 (s, 3H, Pd-CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): *trans*-isomer: 173.39, 156.69, 148.86, 143.60, 141.88, 138.74, 135.41, 135.14, 130.05, 129.44, 129.07, 128.71, 128.51, 128.23, 126.67, 125.55, 124.55, 52.30, 21.74, 16.88, 1.97; *cis*-isomer: 178.78, 152.62, 149.45, 142.70, 141.28, 138.84, 136.35, 135.92, 130.38, 129.65, 129.44, 128.89, 128.51, 128.40, 126.90, 126.69, 124.35, 52.10, 21.74, 17.73, 2.75.

Synthesis of [Pyridine-2-CH=N-Ar]PdMeCl (C2) [Ar = 2,6-bis(diphenylmethyl)-4-methyl]

In a manner similar to that described for C1, complex C2 was obtained as yellow powder in 63% yield. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 9.11 (d, 1H, Py), 7.72 (t, 1H, Py), 7.60 (t, 1H, Py), 7.25–6.94 (m, 20H, Ph), 6.66 (s, 2H, Ar-H), 6.35 (d, 1H, Py), 5.90 (s, 1H, CH), 5.87 (s, 2H, CH), 2.18 (s, 3H, CH₃), 1.01 (s, 3H, Pd-CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): 171.58, 151.21, 149.53, 143.68, 142.33, 142.20, 138.35, 136.75, 136.56, 130.07, 129.38, 128.63, 126.92, 125.67, 52.27, 30.00, 21.83, 1.52.

Synthesis of [(Pyridine-2-C(Me)=N-Ar)PdMe(NCMe)]⁺ BArF[–] (1) [Ar = 2,6-bis(diphenylmethyl)-4-methyl]

The cationic pyridine-imine palladium complex 1 was synthesized by the reaction of NaBArF and acetonitrile with neutral palladium complex C1 in dichloromethane. A typical synthetic procedure for complex 1 can be described as follows: 1.0 mmol of palladium complex C1, 1.2 mmol of NaBArF, and 2 mL of acetonitrile were added to a Schlenk

tube together with 20 mL of dichloromethane, and the reaction mixture was then stirred for 12 h at room temperature. The solution was filtered by Celite and then evaporated under vacuum. Palladium complex **1** as a yellow powder was obtained in 93% yield. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): *cis*-isomer: 8.40 (d, 1H, Py), 7.81 (t, 1H, Py), 7.73 (s, 8H, Ph in BArF[−]), 7.53 (s, 4H, Ph in BArF[−]), 7.33–6.94 (m, 22H, Ph), 6.85 (s, 2H, Ar-H), 5.59 (s, 2H, CH), 2.36 (s, 3H, CH₃), 2.25 (s, 3H, Pd-NCCH₃), 0.93 (s, 3H, CH₃), 0.05 (s, 3H, Pd-CH₃); *trans*-isomer: 8.56 (d, 1H, Py), 7.95 (t, 1H, Py), 7.73 (s, 8H, Ph in BArF[−]), 7.61 (t, 1H, Py), 7.53 (s, 4H, Ph in BArF[−]), 7.33–6.94 (m, 21H, Ph), 6.89 (s, 2H, Ph), 5.53 (s, 2H, CH), 2.25 (s, 3H, CH₃), 1.66 (s, 3H, Pd-NCCH₃), 1.03 (s, 3H, CH₃), 0.72 (s, 3H, Pd-CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm): *trans*-isomer: 174.43, 162.31, 161.32, 156.70, 149.93, 141.68, 141.10, 140.65, 140.07, 137.01, 135.14, 130.21, 129.95, 129.61, 129.26, 129.19, 127.64, 127.01, 126.02, 122.10, 120.82, 53.14, 21.71, 17.20, 4.93, 2.46; *cis*-isomer: 183.05, 162.80, 161.81, 152.00, 148.59, 141.91, 141.29, 140.57, 138.02, 135.96, 135.14, 130.21, 129.54, 129.49, 129.33, 128.83, 127.57, 127.30, 126.24, 123.53, 117.87, 52.70, 21.86, 18.35, 8.43, 3.34.

Synthesis of [(Pyridine-2-CH = N-Ar)PdMe(NCMe)]⁺ BArF[−] (**2**) [Ar = 2,6-bis(diphenylmethyl)-4-methyl]

In a manner similar to that described for **1**, cationic palladium complex **2** as yellow powder was obtained in 96% yield. ¹H-NMR (400 MHz, CDCl₃, δ , ppm): *trans*-isomer: 8.25 (d, 1H, Py), 7.72 (s, 8H, Ph in BArF[−]), 7.65 (t, 1H, Py), 7.53 (s, 4H, Ph in BArF[−]), 7.65 (t, 1H, Py), 7.33–7.30 (m, 5H, Ph), 7.21 (t, 1H, Py), 7.11–7.00 (m, 11H, Ph), 6.91–6.87 (m, 4H, Ph), 6.69 (s, 2H, Ar-H), 6.39 (d, 1H, Py), 5.80 (s, 1H, CH), 5.56 (s, 2H, CH), 2.01 (s, 3H, CH₃), 1.87 (s, 3H, Pd-NCCH₃), 1.13 (s, 3H, Pd-CH₃); *cis*-isomer: 8.42 (d, 1H, Py), 7.83 (t, 1H, Py), 7.72 (s, 8H, Ph in BArF[−]), 7.53 (s, 4H, Ph in BArF[−]), 7.33–7.30 (m, 6H, Ph), 7.11–7.00 (m, 11H, Ph), 6.91–6.87 (m, 4H, Ph), 6.69 (s, 2H, Ar-H), 6.39 (d, 1H, Py), 5.80 (s, 1H, CH), 5.56 (s, 2H, CH), 2.34 (s, 3H, CH₃), 2.20 (s, 3H, Pd-NCCH₃), 1.03 (s, 3H, Pd-CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ , ppm) *trans*-isomer: 175.00, 162.80, 161.81, 152.28, 148.77, 142.86, 140.99, 140.19, 138.31, 136.52, 135.12, 129.82, 129.49, 129.22, 127.48, 126.23, 122.30, 120.81, 53.12, 21.93, 5.40, 2.59; *cis*-isomer: 175.00, 162.80, 161.81, 152.28, 148.77, 142.86, 141.35, 140.19, 138.31, 136.52, 135.12, 129.82, 129.06, 128.98, 127.56, 126.23, 123.52, 117.87, 52.81, 21.93, 6.95, 3.25.

Ethylene Polymerization at Atmosphere Pressure

A round bottom Schlenk flask with stirring bar was heated for 3 h at 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 0.1 MPa of ethylene and vented three times. Toluene was added into the glass reactor under 0.02 MPa of ethylene. The system was continuously stirred for 5 min, and then toluene and 2 mL solution of palladium complex in CH₂Cl₂ were added sequentially by syringe to the well-stirred solution, and the total reaction volume was kept at 30 mL. The ethylene pressure was kept constant at 0.02 MPa by continuous feeding of gaseous ethylene throughout the reaction. The other

reaction temperatures were controlled with an external water bath in polymerization experiments. The polymerizations were terminated by the addition of 2 mL of triethyl silane after continuously stirring for an appropriate period. Solvent in the resulting mixture was removed by vacuum, and the palladium black was centrifugally removed. The product was purified by column chromatography with petrol and dried in vacuum at 75 °C to a constant weight.

Ethylene Polymerization at High Pressure

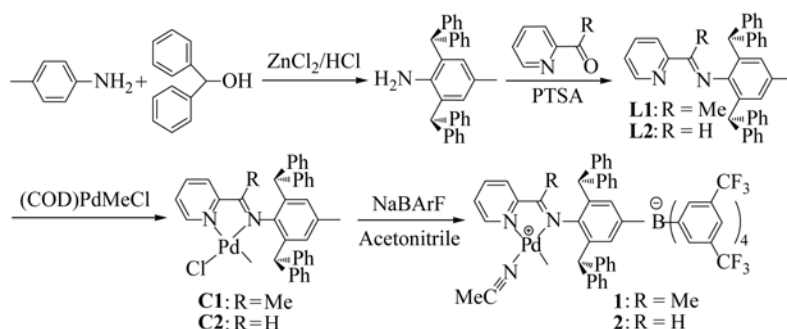
A mechanically stirred 100 mL Parr reactor was heated to 150 °C for 2 h under vacuum and then cooled to room temperature. The autoclave was pressurized to 0.1 MPa of ethylene and vented three times. The autoclave was then charged with toluene under 0.02 MPa of ethylene at initialization temperature. The system was maintained by continuously stirring for 5 min, and then a 2 mL solution of palladium complex in CH₂Cl₂ was charged into the autoclave. The ethylene pressure was raised to the specified value. The reaction temperature was controlled by means of an external water bath. The reaction was carried out for a certain time. The polymerizations were terminated by the addition of 2 mL of triethyl silane after continuously stirring for an appropriate period. Solvent in the resulting mixture was removed by vacuum, and the palladium black was centrifugally removed. The product was purified by column chromatography with petrol and dried in vacuum at 75 °C to a constant weight.

Characterization

NMR spectra of organic compounds and polymers were carried out on a Bruker 400 MHz instrument in CDCl₃ using tetramethyl silane (TMS) as a reference. GPC analysis of the molecular weight and polydispersity (PDI = M_w/M_n) of the polymers at 40 °C was performed on a Breeze GPC chromatograph equipped with a RI detection array; tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. The crystals were mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. Data obtained with the ω -2 θ scan mode was collected on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Cu K α radiation (λ = 1.54178 Å). The structures were solved using direct methods, while further refinement with full-matrix least-squares on F^2 was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

RESULTS AND DISCUSSION

Pyridine-imine ligands were synthesized by condensation reactions between 2-acetylpyridine or pyridine-2-aldehyde with 2,6-bis(diphenylmethyl)-4-methylaniline according to previously reported method^[36, 38]. The new chloromethyl-palladium complexes were obtained by complexation of the ligand and (COD)PdMeCl (COD: 1,5-cyclooctadiene) (Scheme 1). In principle, there are two geometrical isomers (*cis*- and *trans*-isomers) for the chloromethylpalladium complexes bearing pyridine-imine ligands. ¹H- and ¹³C-NMR analysis showed that the obtained palladium complex **C1** was



Scheme 1 Synthesis of pyridine-imine palladium complexes

a mixture of *cis*- and *trans*-isomers with a ratio of 8/1 (Fig. 1). However, only one isomer existed in the solution of complex **C2** (Fig. 2), which might be a result of steric interaction effect on geometrical isomers of the palladium complex. Similar observation was previously reported for pyridine-imine palladium complexes with a 2,6-diisopropylaniline^[52, 53].

Single crystals of chloromethylpalladium complexes **C1** and **C2** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into the palladium complex solution in dichloromethane (Figs. 3 and 4), and crystal data and structure refinement for **C1** and **C2** are summarized in Table 1. Single crystal X-ray diffraction analysis of **C1** and **C2** further confirmed that chloromethylpalladium complexes

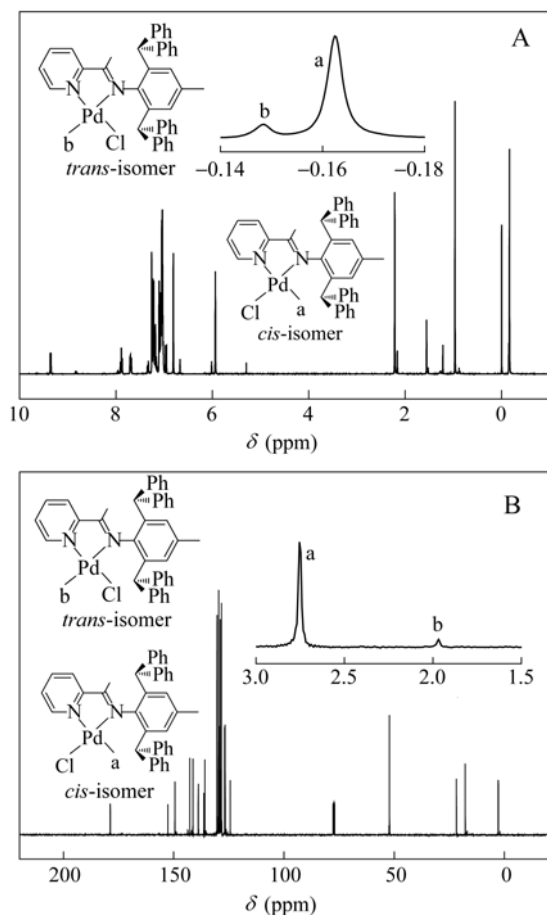


Fig. 1 (A) ¹H- and (B) ¹³C-NMR spectra of pyridine-imine palladium complex **C1**

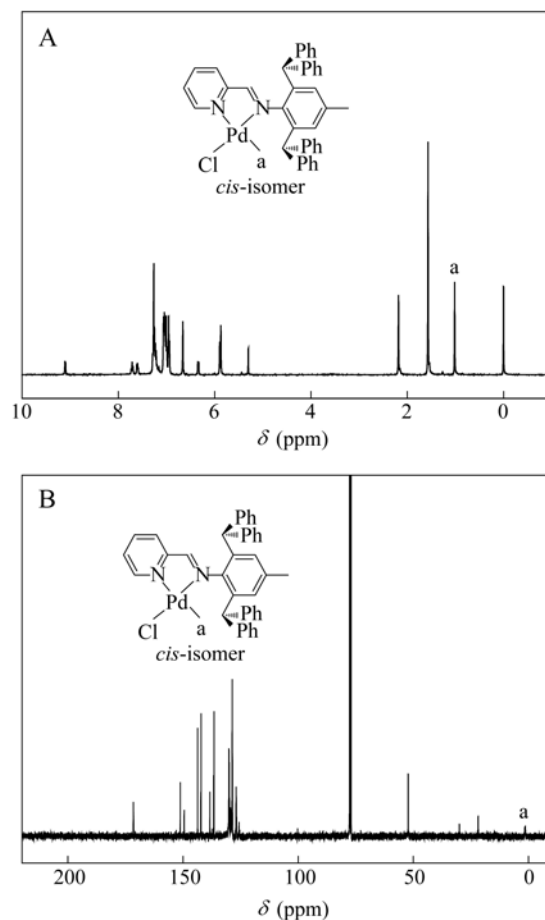


Fig. 2 (A) ¹H- and (B) ¹³C-NMR spectra of pyridine-imine palladium complex **C2**

C1 and **C2** were majorly present as a *trans*-chelate isomer and featured the methyl group *cis*- to the imine group. The *cis*- configuration was also found to be the most favorable for the majority of chloromethylpalladium complexes^[52, 53]. As expected, the geometry about palladium is nearly square-planar, and the angle N(2)–Pd(1)–N(1) is less than 90°. The Pd–N(1) (pyridine) bond length is around 2.13 and 2.15 Å while Pd–N(2) (imine) bond length is around 2.07 and 2.05 Å for **1** and **2**, respectively. This is obviously different to pyridine-imine palladium complex with a 2,6-isopropylaniline (Pd–N(1) (pyridine) bond of 2.04 Å versus Pd–N(2) (imine) bond of 2.09 Å)^[52], suggesting

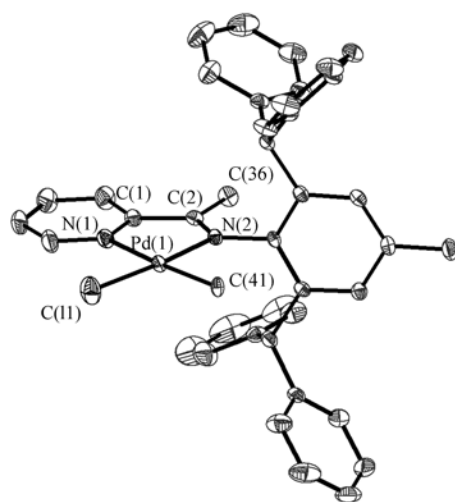


Fig. 3 Molecular structure of **C1** with hydrogen atoms omitted (Selected bond length (Å) and angles (°): Pd(1)—Cl(1) 2.2942(7), Pd(1)—N(1) 2.130(2), Pd(1)—N(2) 2.068(2), Pd(1)—C(41) 2.089(2), N(1)—C(1) 1.348(3), C(1)—C(2) 1.483(3), N(2)—C(2) 1.292(3), C(2)—C(36) 1.492(3), N(1)—Pd(1)—Cl(1) 97.23(6), N(2)—Pd(1)—Cl(1) 174.92(6), N(2)—Pd(1)—N(1) 77.73(8), N(2)—Pd(1)—C(41) 97.11(8), C(41)—Pd(1)—Cl(1) 87.93(7), C(41)—Pd(1)—N(1) 174.83(8), C(1)—N(1)—Pd(1) 113.53(17), C(2)—N(2)—Pd(1) 117.03(17), N(1)—C(1)—C(2) 115.2(2), N(2)—C(2)—C(1) 116.5(2), N(2)—C(2)—C(36) 125.2(2), C(1)—C(2)—C(36) 118.3(2))

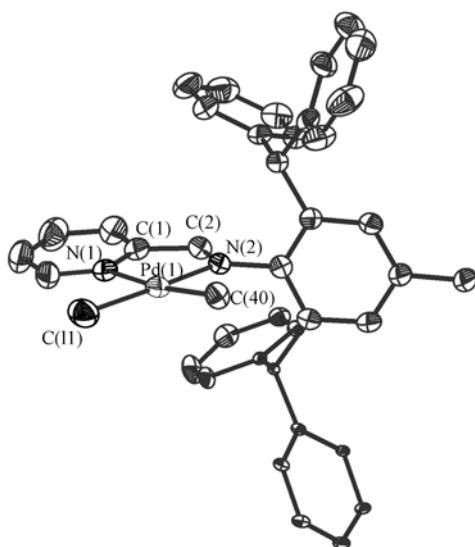


Fig. 4 Molecular structure of **C2** with hydrogen atoms and 0.5 CH₂Cl₂ omitted (Selected bond length (Å) and angles (°): Pd(1)—Cl(1) 2.2955(15), Pd(1)—N(1) 2.153(5), Pd(1)—N(2) 2.051(5), Pd(1)—C(40) 2.109(5), N(1)—C(1) 1.340(7), N(2)—C(2) 1.269(7), C(1)—C(2) 1.473(7), N(1)—Pd(1)—Cl(1) 97.51(13), N(2)—Pd(1)—Cl(1) 175.87(14), N(2)—Pd(1)—N(1) 78.39(18), N(2)—Pd(1)—C(40) 94.53(19), C(40)—Pd(1)—Cl(1) 89.60(15), C(40)—Pd(1)—N(1) 172.13(19), C(1)—N(1)—Pd(1) 111.9(3), C(2)—N(2)—Pd(1) 115.3(3), N(1)—C(1)—C(2) 114.5(5), N(2)—C(2)—C(1) 119.5(5))

Table 1 Crystal data and structure refinement for palladium complexes **C1** and **C2**

	C1	C2
Empirical formula	C ₄₁ H ₃₇ ClN ₂ Pd	C ₈₀ H ₇₀ Cl ₂ N ₄ Pd ₂ • CH ₂ Cl ₂
Formula weight	699.57	1456.03
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
<i>a</i> (Å)	9.3757(3)	39.1381(8)
<i>b</i> (Å)	12.8254(4)	9.3832(3)
<i>c</i> (Å)	14.5087(4)	19.7923(4)
α (°)	85.737(2)	90
β (°)	84.994(2)	112.916(2)
γ (°)	73.818(2)	90
Volume (Å ³)	1666.84(9)	6694.9(3)
<i>Z</i>	2	4
<i>D</i> (calc.) (g/cm ³)	1.394	1.445
<i>F</i> (000)	720	2984
Crystal size (mm × mm × mm)	0.35 × 0.30 × 0.25	0.25 × 0.20 × 0.20
θ range (°)	3.593 to 73.945	4.503 to 74.170
Index ranges	−10 ≤ <i>h</i> ≤ 11 −15 ≤ <i>k</i> ≤ 12 −17 ≤ <i>l</i> ≤ 17	−48 ≤ <i>h</i> ≤ 46 −11 ≤ <i>k</i> ≤ 10 −24 ≤ <i>l</i> ≤ 23
Reflections collected/unique	11609/6518	30742/6708
	[<i>R</i> (int) = 0.0398]	[<i>R</i> (int) = 0.0466]
Data completeness	99.8%	100%
Data/restraints/parameters	6518/0/409	6708/85/472
Goodness-of-fit on <i>F</i> ²	1.042	1.134
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0349, <i>wR</i> ₂ = 0.0956	<i>R</i> ₁ = 0.0687, <i>wR</i> ₂ = 0.1672
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0354, <i>wR</i> ₂ = 0.0961	<i>R</i> ₁ = 0.0703, <i>wR</i> ₂ = 0.1682
Largest diff. peak and hole (e/Å ³)	0.904 and −1.010	2.370 and −1.213

that bulky benzhydryl groups enhanced donor ability of imine. The aryl ring of aniline moiety is nearly perpendicular to the five-membered chelating plane, which provides one-side axially steric bulk.

The pyridine-imine chloromethylpalladium complexes were further treated with sodium tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate (NaBARF) and acetonitrile to yield the cationic palladium complexes^[16, 33]. ¹H- and ¹³C-NMR spectroscopies clearly showed that cationic palladium complexes **1** and **2** existed two geometrical isomers (*cis*- and *trans*-isomers) in the solution. The ratios of *cis*-isomer to *trans*-isomer were separately calculated to 2.5/1 and 8/1 for **1** and **2** under the measured conditions (Figs. 5 and 6). Although there were two isomers in solution, the same palladium active species with ethylene monomer *cis*- to the imine group was expected because of steric interaction effect between growing PE chain with *ortho* dibenzhydryl groups^[36–39].

Cationic palladium complexes **1** and **2** can polymerize ethylene without any cocatalysts. The ethylene polymerization results using palladium catalysts **1** and **2** under various conditions are summarized in Table 2. Under atmosphere pressure, catalyst **1** showed the highest activity

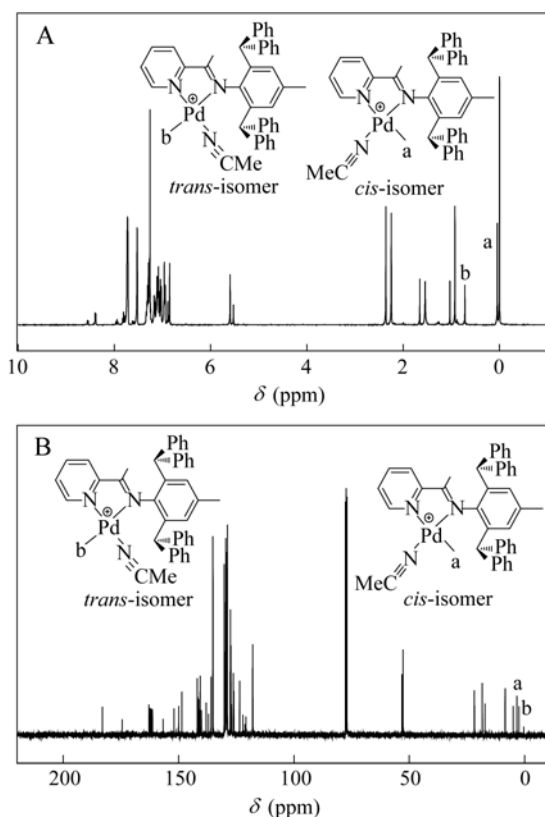


Fig. 5 (A) ^1H - and (B) ^{13}C -NMR spectra of cationic pyridine-imine palladium complex **1**

31.3 kgPE/(molPd·h) at 45 °C. When the reaction temperature was increased from 45 °C to 55 °C, the polymerization activity slightly decreased. Importantly, the palladium black generating from the decomposition of the palladium catalysts in the polymerization mixture was not observed for catalyst **1** below 55 °C, whereas it usually appeared for palladium catalysts above room temperature^[16, 33]. These results indicated good thermal stability of pyridine-imine palladium catalyst **1**. Increasing ethylene pressure from 0.02 MPa to 1 MPa for catalysts **1** and **2** led to an increasing activity whereas the product molecular weight was nearly unchanged. Figure 7 shows that the catalytic activity is nearly unchanged with prolonging reaction time, suggesting that the palladium catalyst **1** is stable at 45 °C over a 12 h-period under the adopted conditions.

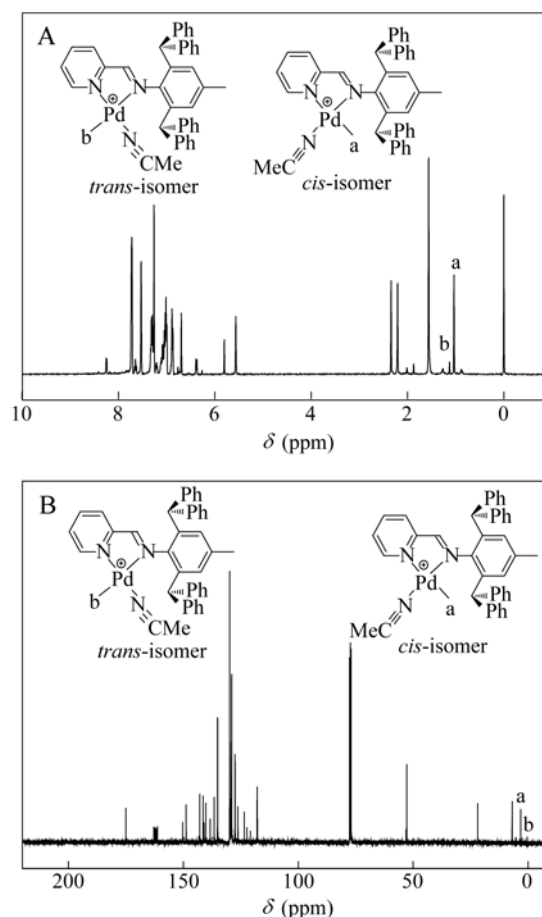


Fig. 6 (A) ^1H - and (B) ^{13}C -NMR spectra of cationic pyridine-imine palladium complex **2**

In contrast to the previous work on pyridine-imine palladium with a 2,6-diisopropylaniline, catalyst **1** showed higher activity and afforded polymeric product with higher molecular weight^[52]. The enhanced catalytic activity, thermal stability, and molecular weight of catalyst **1** were ascribed to the introduction of bulky benzhydryl on the *ortho* position of aniline^[41, 51, 52].

Substituents on the bridging carbon also played an important role in the ethylene polymerization with pyridine-imine catalysts. Compared with catalyst **1**, catalyst **2** without substituents on the bridging carbon was less effective in ethylene polymerization. Under the same conditions, a

Table 2 Ethylene polymerizations with pyridine-imine palladium catalysts^a

Entry	Catalyst	T (°C)	Pressure (MPa)	Yield (g)	Act. ^b	M_n ^c (g/mol)	PDI ^c	BD ^d
1	1	35	0.02	2.07	25.9	755	1.10	112
2	1	45	0.02	2.50	31.3	759	1.11	136
3	1	55	0.02	1.92	24.0	738	1.11	142
4	1	45	0.5	7.94	99.3	751	1.12	116
5	1	45	1	9.17	114.6	741	1.11	115
6	2	35	0.02	1.34	16.7	613	1.03	183
7	2	45	0.02	1.58	19.8	639	1.04	194
8	2	55	0.02	1.70	21.3	626	1.05	210
9	2	45	0.5	2.10	26.3	585	1.10	116
10	2	45	1	2.47	31.0	586	1.10	115

^a Conditions: 20 μmol Pd, 28 mL toluene and 2 mL CH_2Cl_2 , polymerization time 4 h; ^b Activity in kgPE/(molPd·h); ^c Determined by gel permeation chromatography; ^d Branching degree, determined by ^1H -NMR spectroscopy.

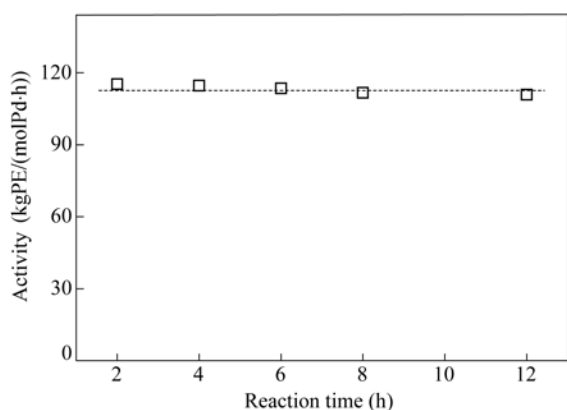


Fig. 7 Plots of activity versus reaction time in ethylene polymerization using **C1** under 45 °C and 1 MPa ethylene pressure

remarkable decrease in the catalytic activity and molecular weight was observed when methyl was removed from the bridging carbon. This was reasonably attributed to accelerating chain transfer reaction with less bulky substituent on the bridging carbon^[41, 43]. However, reducing the steric bulk on the bridging carbon from methyl to hydrogen leads to a significant increase in the total branching degree. This observation is similar to those reported for polymers produced using the pyridine-amine nickel complexes^[36, 38]. Therefore, modification of substituents on *ortho* position of aniline moiety and bridging carbon can provide a viable access to tuning the molecular weight and branching degree of the obtained products.

Due to one-side steric hindrance of pyridine-imine palladium catalysts, the low-molecular-weight products were produced as we envisioned^[51–53]. The obtained products were transparent colorless oil with low molecular weight of 600–800 g/mol determined by gel permeation chromatography (GPC). ¹H-NMR analysis showed all of the obtained products were highly branched (> 100/1000C) and branching density was insensitive to the reaction temperature and ethylene pressure. ¹³C-NMR spectrum of the oligomer shown in Fig. 8 further revealed that methyl and ethyl were present^[54–57]. In addition, the branch-on-branch structure generated through tertiary carbons, specially a *sec*-butyl branch (11.59 and 19.41 ppm) was also formed. Low-molecular-weight and high branching density are cooperatively responsible for oil product. This polyethylene oil may have a potential application in the areas of lubricant^[58, 59].

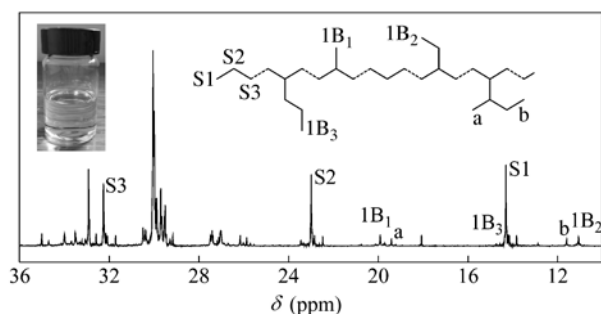


Fig. 8 ¹³C-NMR spectrum of the obtained oligomer (Table 2, entry 5)

CONCLUSIONS

In summary, we have successfully synthesized and characterized pyridine-imine palladium complexes with dibenzhydryl substituents. Cationic pyridine-imine palladium complexes were capable of catalyzing ethylene oligomerization with good activities. The introduction of bulky benzhydryl on the *ortho* position of aniline moiety enhanced catalytic activity, thermal stability of the catalyst, and molecular weight of the obtained products. In addition, increasing bulk on the bridging carbon led to a remarkable increase in the catalytic activity and molecular weight but a reducing branching degree of the obtained product. The obtained oligomers were highly branched and present as transparent colorless oil, which may have a potential application in the areas of lubricant.

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