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A thermal stable α-diimine palladium catalyst for copolymerization of ethylene with functionalized olefins

Huijie Pan[1], Liang Zhu[1], Jiewei Li, Dandan Zang, Zhisheng Fu*, Zhiqiang Fan

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

Copolymerization of polar monomers and olefins catalyzed by transition metal under mild conditions is a challenge. α-Diimine palladium complexes have great potential to catalyze the copolymerization of alkylacrylates and olefins. But they are prone to deactivation under mild conditions which limits their industrial application. A novel unsymmetrical α-diimine palladium complex with bulkier α-diimine ligand was provided in this paper. They were active in ethylene homopolymerization at 80 °C. At 50 °C they could produce ethylene/methylacrylate copolymer with moderate methylacrylate incorporation. The probable reason for the high thermal stability of these complexes was proposed.

1. Introduction

Compared with polyolefins, polar polyolefin copolymers show better properties, such as mar resistance, toughness and printing properties. They are commercially manufactured by free radical polymerization under very harsh conditions with branched structures and broad molecular weight distributions [1,2]. It is difficult to control the copolymer composition [3]. Coordination polymerization catalyzed by transition metal would permit the synthesis of polar polyolefin copolymers under mild conditions, reduce production costs and allow better control of their composition and microstructure. Therefore, for many years an intense research effort to overcome the difficulties in controlling the copolymerization of polar monomers and olefins has been sustained [2,4–7]. In 1995 Brookhart found that α-diimine palladium complexes could catalyze the copolymerization of ethylene with alkylacrylates [8,9]. It encouraged researchers to develop novel α-diimine palladium catalysts that could copolymerize polar monomers and olefins [10–21]. However, α-diimine palladium catalysts are prone to deactivation under mild conditions in comparison to Ziegler-Natta catalysts. Brookhart et al. demonstrated that the deactivation took place by C—H activation with alkyl groups on the α-diimine ligand to form palladacyclic intermediates (Scheme 1) [22]. But those α-diimine palladium complexes bearing 2,6-diphenyl aniline moieties (complex **1**, as shown in Fig. 1) whose aniline-phenyl groups without alkyl could not rotate freely around their N—C_{arom} bond decomposed within minutes during the polymerization reaction [23]. The other α-diimine palladium complexes bearing bulky ligands, such as cyclophane-based Pd(II) α-diimine palladium catalysts [24] and camphyl α-diimine palladium catalyst [25], generally catalyze the copolymerization of ethylene with alkylacrylates below 35 °C with low activity. However, in terms of prospective commercialization, such catalysts would typically need to operate at temperatures of between 80 and 100 °C [26].

Since the α-diimine nickel complexes bearing 2,6-diphenyl aniline moieties (the analogue of complex **1**) exhibited unprecedentedly high activity at ambient temperature [23], C—H activation might be not the only reason for the deactivation of the corresponding α-diimine palladium complexes. Because the α-diimine ligand in complex **1**was a large and rigid molecule, the push and squeeze of the ligand around the metal center might be the other reason. The vibration and fluctuation of the methyl groups on the backbone of the ligand in complex **1** will repel the substituents bonded to the imine groups. And finally the repulsion will be conducted to the metal center. Nickel has a smaller atomic radius (0.1243 nm) than palladium (0.1376 nm). Therefore, nickel complexes are stable while palladium complexes are unstable.

In this paper, two methyl groups on the backbone and one 2,6-diphenyl aniline moiety were replaced by a naphthyl group and a

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* Corresponding author. Tel.: +86 571 87953754.
E-mail address: fuzs@zju.edu.cn (Z. Fu).

[1] These authors contributed equally.

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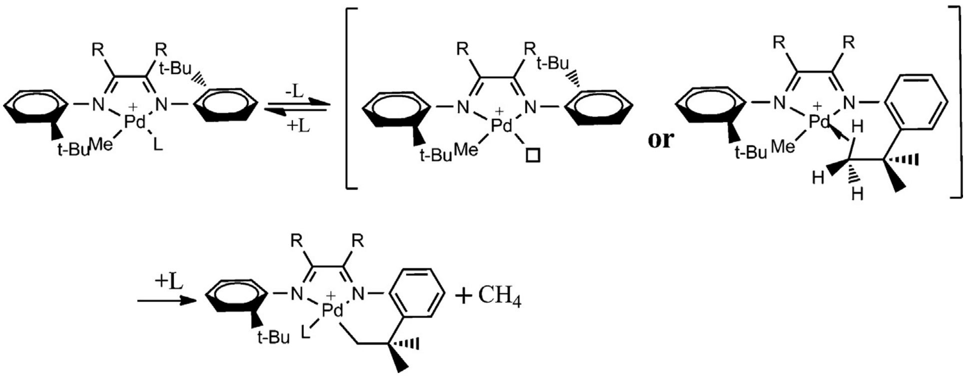


Scheme 1. Possible intermediates for palladacycle formation via α-diimine C—H activation [22].

2,6-diisopropyl aniline, respectively, to afford a novel unsymmetric α-diimine palladium complex**2** (Fig. 1). The ethylene homopolymerization and ethylene/methylacrylate (MA) copolymerization catalyzed by complex **2** were investigated.

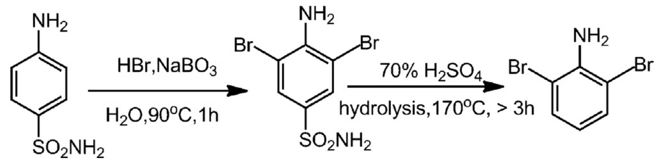
2. Experimental

All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques.

2.1. Materials

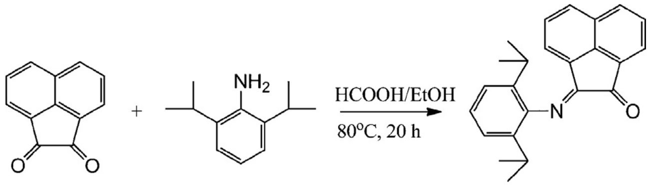
Toluene, diethyl ether and hexane were purified by refluxing and distillation over sodium, and kept under a dry nitrogen atmosphere. Methylene chloride was purified by refluxing and distillation over CaH_2, and kept under a dry nitrogen atmosphere. Methylene chloride-d_2 was dried by distillation over P_2O_5, vacuum-transferred and stored in the dry box. Methyl acrylate (MA) was distilled to remove radical inhibitor, stored over 4 Å molecular sieves and purged with nitrogen prior to use. Phenylboronic acid, *p*-tert-butyl phenylboronic acid and *p*-methoxyphenylboronicacid were purchased from Frontier Scientific and used as received. 2,6-Diisopropyl aniline (Acros) and acenaphthequinone (Alfa Aesar) were used as received. The synthesis and characterization of (COD)PdMeCl [1] has been previously reported.

2.2. Synthesis of 2,6-dibromoaniline



To a mixture of 50.0 g sulfanilamide, 850 mL water and 200 mL 48% HBr solution, 90.0 g sodium perborate was added at 85 °C. The mixture was stirred at 80–85 °C for 30 min and then was cooled to room temperature and filtered. The residue was washed to be neutral by water. The solid was desulfonated by reacting with 70% sulfuric acid solution for 3 h under reflux. Crude product was obtained by steam distillation and further purified by recrystallization in ethanol. ^1H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.35–7.40 (d, 2H, Ar-H_m), 6.5 (t, 1H, Ar-H_p).

2.3. Synthesis of 2-[(2,6-diisopropylphenyl)imino]acenaphthylen-1-one



2,6-Diisopropyl aniline (1.45 g, 8.22 mmol) dissolved in ethanol (50 mL) was added slowly to a mixture of acenaphthequinone (2.0 g, 11.0 mmol) with ethanol (65 mL) at 60 °C. The catalytic amount

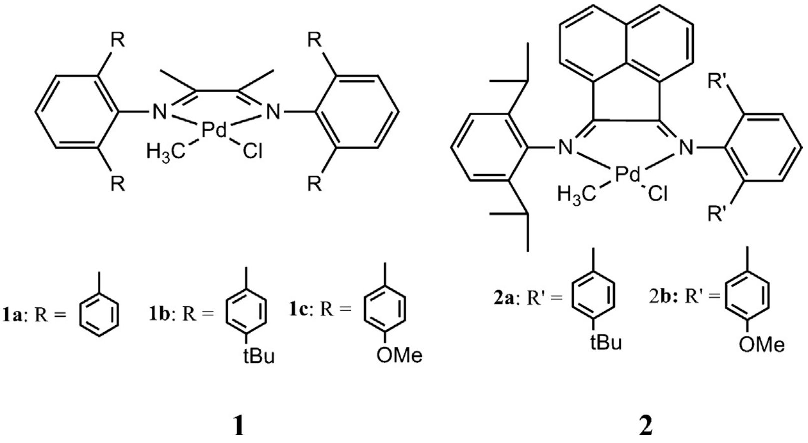


Fig. 1. α-Diimine palladium complexes bearing 2,6-diphenyl aniline moieties.

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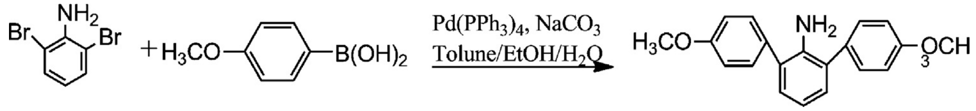
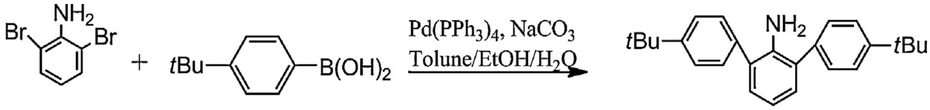
of formic acid (1 mL, 26.5 mmol) was added. The solution was heated to under reflux for 20 h. Unreacted acenaphthequinone was removed by filtration at room temperature. The filtrate was further purified by column chromatography (silica gel, ethyl acetate:hexane = 1:16) to give an orange red solid (1.68 g, yield 60%).^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 8.20 (d, 1H, An-H_o), 8.17 (d, 1H, An-H_p), 7.98 (d, 1H, An-H_o), 7.41 (t, 1H, An-H_m), 7.26 (m, 3H, Ar-H), 6.64 (d, 1H, An-H_p), 2.84 (sept, 2H, $CH(CH_3)_2$), 1.18 (d, 6H, $CH(CH_3)_2$), 0.91 (d, 6H, $CH(CH_3)_2$).

2.4. Synthesis of 2,6-di(4-methoxy)phenylaniline



4-methoxy phenylboronic acid (2.72 g, 18 mmol) dissolved in ethanol (12 mL) and 2 M Na_2CO_3 (24 mL, 48 mmol) were added to a solution of 2,6-dibromoaniline (1.56 g, 6 mmol) in toluene (60 mL). To this solution, $Pd(PPh_3)_4$ (0.84 g, 0.67 mmol) was added. The solution was heated to reflux for 72 h. After cooling to room temperature, the mixture was filtered and an excess of aqueous HCl was slowly added to the filtrate until no more white solid precipitated. The residue was suspended in diethyl ether after filtration, and then an excess of 2 M Na_2CO_3 was slowly added until the solid was totally dissolved. The organic layer was dried over Na_2SO_4 and then the solvent was removed to give light yellow solid (1.10 g, yield 60.3%). ^{1}H NMR (500MHz, $CDCl_3$, δ in ppm): 7.45 (d, 4H, Ar-H_m), 7.10 (d, 2H, Ar-H_m), 7.00 (d, 4H, Ar-H_m), 6.85–6.90 (t, 1H, Ar-H_p), 3.85–3.88 (s, 6H, OCH_3).

2.5. Synthesis of 2,6-di(4-tert-butyl)phenylaniline



4-tert-Butylphenylboronic acid (4.81 g, 27.0 mmol) dissolved in ethanol (18 mL) and 2 M Na_2CO_3 (36 mL, 72 mmol) were added to a solution of 2,6-dibromoaniline (2.258 g, 9.0 mmol) in toluene (90 mL). To this solution, $Pd(PPh_3)_4$ (1.26 g, 1.0 mmol) was added. The mixture was heated to reflux for 72 h. After cooling to room temperature, the mixture was filtered and an excess of aqueous HCl was slowly added to the filtrate until no more white solid precipitated. The residue was suspended in diethyl ether after filtration and then an excess of 2 M Na_2CO_3 was slowly added until the solid was totally dissolved. The organic layer was dried over Na_2SO_4 and then the solvent was evaporated to give white solid (1.80 g, yield 56%). ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.47–7.52 (m, 8H, Ar-H_m), 7.15 (d, 2H, Ar-H_o), 6.89 (t, 1H, Ar-H_p), 3.95 (s,2H, NH_2), 1.40 (s, 18H, CH_3).

2.6. Synthesis of Ligand **2a**

Triethylene-diamine (1.33 g, 12 mmol) was added to a solution of 2,6-di(4-tert-butyl)phenylaniline (1.43 g, 4.0 mmol) in chlorobenzene (20 mL). To this solution, a solution of $TiCl_4$ (0.8 mL, 7.3 mmol) in chlorobenzene (2 mL) (Scheme 2) was slowly added at 90 °C. Then 2-[(2,6-diisopropylphenyl)imino]acenaphthylen-1-one (0.68 g, 2.0 mmol) dissolved in chlorobenzene (6.0 mL) was added at once. The mixture was stirred at 150 °C for 48 h. The solvent was removed in vacuum and the residue was dissolved in CH_2Cl_2. After filtration, the solution was concentrated and purified by chromatography (silica gel, CH_2Cl_2/Hexane/EtOAc = 40/40/1) to give a yellow solid (0.64 g, yield 47.1%).^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.82 (d, 1H, An-H_o), 7.78 (d, 1H, Ar-H_o), 7.38–7.52 (m, 8H, Ar-H), 7.18–7.29 (m, 8H, Ar-H), 6.90 (d, 1H, An-H_m), 6.39 (d, 1H, An-H_p), 2.84 (sept, 2H, $CH(CH_3)_2$), 1.23 (s, 18H, CH_3), 1.22 (d, 6H, $CH(CH_3)_2$), 0.78 (d, 6H, $CH(CH_3)_2$). Anal. Calcd. for $C_{50}H_{52}N_2$: C, 88.19; H, 7.70; N, 4.11. Found: C, 87.82; H, 7.78; N, 4.21.

2.7. Synthesis of Ligand **2b**

Scheme 2 showed the synthesis route of α-diimine palladium catalysts. Triethylene-diamine (0.267 g, 2.4 mmol) was added to a solution of 2,6-di(4-methoxy)phenylaniline (0.286 g, 0.8 mmol) in chlorobenzene (9 mL). To this solution, a solution of $TiCl_4$ (0.2 mL, 1.8 mmol) in chlorobenzene (2 mL) was slowly added at 90 °C. Then 2-[(2,6-diisopropylphenyl)imino]acenaphthylen-1-one (0.204 g, 0.4 mmol) dissolved in chlorobenzene (3.5 mL) was added at once. The mixture was stirred at 150 °C for 48 h. The solvent was removed in vacuum and the residue was dissolved in CH_2Cl_2. After filtration, the solution was concentrated and purified by chromatography (silica gel, CH_2Cl_2/Hexane/EtOAc = 40/40/1) to give a yellow solid (0.16 g, yield 63.6%). ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.85 (d, 1H, An-H_o), 7.75 (d, 1H, Ar-H_o), 7.74–7.75 (m, 8H, Ar-H), 7.20–7.30 (d, 4H, Ar-H_m), 6.87 (d, 1H, An-H_m), 6.72 (d, 4H, Ar-H_m), 6.39 (d, 1H, An-H_p), 3.72 (s, 6H, OCH_3), 2.84 (sept, 2H, $CH(CH_3)_2$), 1.22 (d, 6H, $CH(CH_3)_2$), 0.78 (d, 6H, $CH(CH_3)_2$). Anal. Calcd. for $C_{44}H_{40}N_2O_2$: C, 84.04; H, 6.41; N, 4.46. Found: C, 83.11; H, 6.59; N, 4.39.

2.8. Synthesis of complex **2a**

A solution of ligand **2a** (0.30 g, 0.44 mmol) in CH_2Cl_2 (10 mL) was added to a solution of (COD)PdMeCl (0.11 g, 0.42 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at 25 °C for 24 h. The solvent was removed in vacuum and the residue was washed with diethyl ether (3 × 10 mL). The residue was evaporated in vacuum to give an orange powder (0.32 g, yield 91.1%). Anal. Calcd. for $C_{51}H_{55}N_2ClPd$: C, 73.11; H, 6.62; N, 3.34. Found: C, 71.62; H, 6.77; N, 3.19.

Single crystals of complex **2a** suitable for X-ray diffraction analysis were obtained by laying hexane on the dichloromethane solution at −10 °C. With graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173(2) K, cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [27].

2.9. Synthesis of complex **2b**

A solution of ligand **2b** (0.30 g, 0.48 mmol) in CH_2Cl_2 (10 mL) was added to a solution of (COD)PdMeCl (0.12 g, 0.45 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at 25 °C for 24 h. The solvent was removed in vacuum and the residue was washed with diethyl ether

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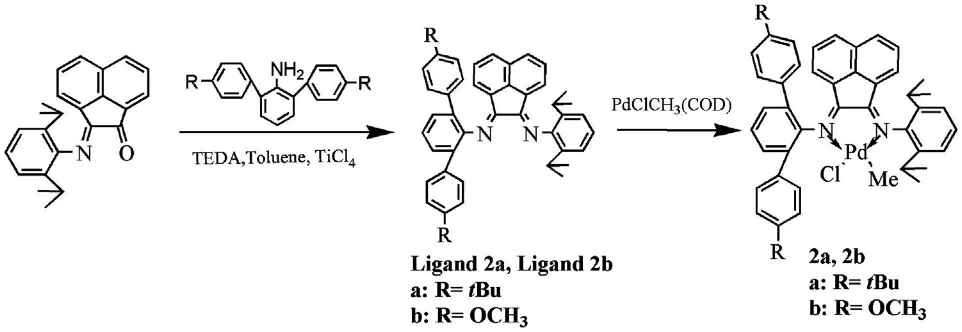

Scheme 2. The synthesis route of α-diimine palladium catalysts.

(3 × 10 mL). The residue was evaporated in vacuum to give a red powder (0.32 g, yield 89.4%). Anal. Calcd. for $C_{45}H_{43}N_2O_2ClPd$: C, 68.68; H, 5.51; N, 3.56. Found: C, 68.54; H, 6.11; N, 3.42.

2.10. General procedure for ethylene homo-polymerization and ethylene/methyl acrylate co-polymerization

A 50 mL Schlenk flask was heated by heat-gun (300–350 °C) under vacuum for more than 5 min, purged with ethylene three times, and immersed into oil-bath at the designated temperature. To this flask, 9 mL of dry toluene was added by syringe, and 0.1 MPa of ethylene was introduced. As to ethylene/methyl acrylate copolymerization, a designated amount of methyl acrylate was added by syringe at this moment. A 10 mL Schlenk flask was heated by heat-gun (300–350 °C) under vacuum for more than 5 min then thrice purged with N_2 and cooled to room temperature. The flask was transferred into dry box and charged with 10 μmol of complex **2a** or **2b** and10 μmol of $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$. To this flask, 1 mL of dry toluene was added. The catalyst solution was then transferred into the 50 mL Schlenk flask by cannula. The polymerization was carried out for a designated time. The resultant polymer solution was filtered through Celite. The filtrate was dried by rotary evaporation. Finally, the resultant polymer was dried in vacuum at 60 °C overnight.

2.11. Characterization

^{1}H NMR spectra of ligands and catalysts were recorded on a Bruker Avance DMX500. ^{1}H NMR spectra of polymers were conducted at room temperature on a Bruker Avance DMX400. All NMR chemical shifts are reported as δ in parts per million (ppm). ^{1}H NMR spectra are reported relative to residual solvent. Elemental analysis (EA) was conducted on a Thermo Electron SPA EA1112. Molecular weights of polymers were determined using a Waters 1515 Gel Permeation Chromatographer with a Waters 2414 differential refractometer in THF.

3. Results and discussion

3.1. Synthesis and characterization of ligands and complexes

As shown in Scheme 3, the condensation reaction of acenaphthene with one equivalent of 2,6-diisopropyl aniline led to **C1**. The bromination and then hydrolysis reactions of sulfanilamide generated 2,6-dibromoaniline. The Suzuki reactions of 2,6-dibromoaniline with various phenylboronic acids led to terphenyl anilines (**C2**). The condensation reaction of **C1** with **C2** led to α-diimine ligands **2a** and **2b**. Ligand **2a** or **2b** reacted with $[(COD)Pd(CH_3)Cl]$ (COD = η^2,η^2-cycloocta-1,5-diene) to form palladium complexes **2a** or **2b** in good yields.

Table 1
Selected bond lengths (**Å**) and angles (degree) for complex **2a**.

	Bond lengths (**Å**)		Bond Angles (°)
Pd(1)—N(1)	2.069	Cl(1)—Pd(1)—C(51)	84.41
Pd(1)—N(2)	2.195	Pd(1)—N(1)—C(9)	128.00
Pd(1)—Cl(1)	2.266	Pd(1)—N(2)—C(25)	132.08
Pd(1)—C(51)	2.097	N(1)—Pd(1)—N(2)	78.70
N(1)—C(13)	1.291	Pd(1)—N(1)—C(13)	110.63
N(1)—C(9)	1.436	Pd(1)—N(2)—C(14)	114.24
N(2)—C(14)	1.276	N(1)—C(13)—C(14)	118.07
N(2)—C(25)	1.434	N(2)—C(14)—C(13)	118.10

A single crystal of palladium complex **2a** suitable for X-ray diffraction analysis was obtained by slow diffusion of hexane into methylene chloridesolution of **2a**. The molecular structure of **2a** was analyzed by single-crystal X-ray diffraction. The molecular structure of **2a** is shown in Fig. 2, and the selected bond lengths and angles are tabulated in Table 1. The crystal, intensity collection, and refinement data for complex **2a** were presented in Table 2. Fig. 2 shows the perspective of the molecular structure along the square plane of the complex. As shown in Fig. 1, each side of the two N-aryl rings lies roughly perpendicular (85.5° and 95.2°) to the molecular

Table 2
Crystallographic Data for Complex**2a**.

Parameters	Data
Empirical formula	$C_{51}H_{55}N_2PdCl$
Formula W_t	837.9
Temp. (K)	140
a(Å)	11.7297(3)
b(Å)	19.8691(4)
c(Å)	19.8742(4)
α(deg)	90.00
β(deg)	95.700(2)
γ(deg)	90.00
V(Å^3)	4608.9(2)
Z	4
D_t(Mg/m$_3$)	1.330
Abs coeff (mm^{-1})	0.613
F(0 0 0)	1920
Crystal size (mm)	0.29 × 0.39 × 0.45
θ range (deg)	3.24–25.35
Index ranges	h: −14 to 12 k: −23 to 18 l: −23 to 17
Completeness	0.998
Absorption correction	Multi-scan
Goodness-of-fit on F^2	1.060
Final R indices	R1 = 0.0572 wR2 = 0.1657
R indices (all data)	R1 = 0.0719 wR2 = 0.1527

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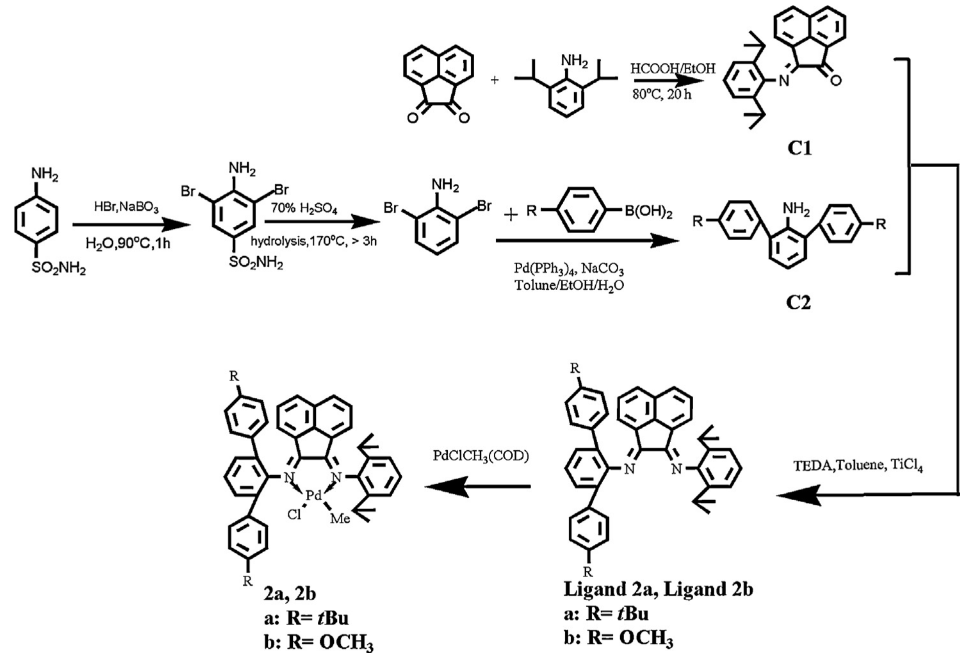

Scheme 3. The total synthesis route of complex **2**.

plane. This structure is critical to block the axial sites and generate high molecular weight polymers.

3.2. *Ethylene homopolymerizations catalyzed by complex **2***

Since complex **1** decomposed within minutes during the polymerization reaction, firstly the stability of complex **2** was tested. The ethylene homopolymerization with 10 μmol of complex **2a** at 0.1 MPa, 25 °C for 2 h yielded 0.1224 g of polyethylene (Table 1, entry 1). As the polymerization time was prolonged to 6.5 h, 0.3244 g of polyethylene was obtained (Table 1, entry 2). It indicated that the lifetime of complex **2a** for polymerization reaction was longer than 2 h. Namely, unlike complex **1**, complex **2a** was stable and did not decompose within minutes during the polymerization reaction. Compared with Brookhart's research results [8], the catalytic activity of complex **2a** was lower than that of the classical (α-diimine) palladium catalyst probably due to the relatively higher steric hindrance of the ligand.

As shown in Table 3, raising the polymerization temperature to 50 °C resulted in slight increase in catalytic activity (5.8×10^3 gPE/molPd•h, Table 3, entry 3). Further raising the temperature to 80 °C did not significantly affect the catalytic

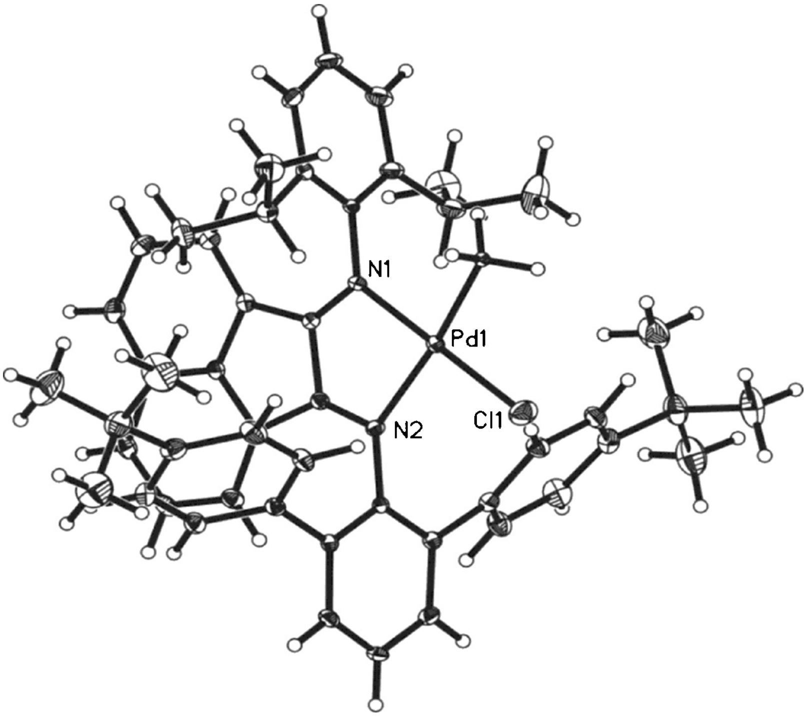

Fig. 2. Molecular structure of depicted with 30% thermal ellipsoids and with hydrogen atoms omitted.

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Table 3
Ethylene homopolymerization catalyzed by complex 2[a].

Entry	Condition	Yield (g)	Activity[b]	Branches[c]	$M_w \times 10^4$	M_w/M_n
1	**2a**, 25 °C, 2 h	0.1224	6.1	-	-	-
2	**2a**, 25 °C, 6.5 h	0.3244	5.0	-	5.64	1.46
3	**2a**, 50 °C, 6.5 h	0.3771	5.8	107	3.41	1.61
4	**2a**, 80 °C, 6.5 h	0.3642	5.6	128	1.48	2.12
5	**2b**, 50 °C, 6.5 h	0.3901	6.0	104	4.10	1.42

[a] Polymerization condition: 10 μmol complex **2**, 10 μmol cocatalyst ($Li(Et_2O)_{2.8}B(C_6F_5)_4$), 10 mL toluene, 0.1 MPa ethylene.
[b] $\times 10^3$ gPE/molPd•h.
[c] CH_3/1000 C, number of methyl group per 1000 carbons determined by ^{1}H NMR.

activity (5.6×10^3 gPE/molPd•h, Table 3, entry 4). As temperature increased, the branches of the resultant polyethylene increased obviously, at the same time, the molecular weights of the resultant polyethylene dropped significantly and the molecular weight distributions of polyethylene broadened to some extent. Complex **2b** was also stable at 50 °C and produced polyethylene with catalytic activity of 6.0×10^3 gPE/molPd•h (Table 3, entry 5).

*3.3. Ethylene/methyl acrylate copolymerizations catalyzed by complex **2***

Since complex **2** was stable and could efficiently catalyze ethylene polymerization at the temperature higher than 35 °C, ethylene/methyl acrylate copolymerizations catalyzed by complex **2** were further investigated.

As shown in Table 4, complex **2** was also stable and produced ethylene/methylacrylate (MA) copolymer with moderate MA incorporation at 25 °C. As expected, the fraction of MA incorporation was directly proportional to its concentration in the reaction solution (entries 1′–3′ and entries 5′–7′). Interestingly, as the copolymerization temperature increased from 25 to 50 °C, both polymerization activity and MA incorporation increased (entries 3′, 4′ and entries 7′, 8′). Especially, complex **2b** afforded copolymer of 4.03 mol% MA at 50 °C, which was almost twice that at 25 °C. At the same time, the catalytic activity of complex **2b** at 50 °C was also twice that at 25 °C. During the copolymerization, a six-membered chelate complex is formed after insertion of MA (as shown in Scheme 4). Further chain growth requires coordination and insertion of ethylene. This is the turnover-limiting step. Therefore, the chelate complex is the catalyst resting state [9]. Probably, raising the polymerization temperature resulted in the activation of the six-membered chelate complex. Namely, the higher the polymerization temperature, the more readily the six-membered chelate complex could open. Thus, raising the polymerization temperature resulted in an increase in ethylene and MA turnovers.

*3.4. The probable reason for thermal stability of complex **2***

For deactivation in α-diimine metal catalysts, a possible reason has been proposed that the metal center reacts with the C—H bonds of the *ortho*-aryl substituents on aniline moiety (C—H activation) to give a six-membered metallacycle [22]. However, complex **1** did not possess *ortho*-aryl alkyl substituents. Using complex **1** to catalyze ethylene polymerization at room temperature in CH_2Cl_2, it decomposed quickly during the polymerizationreaction [23]. On the contrary, complex **2** who possessed *ortho*-isopropyl could catalyze ethylene polymerization at 80 °C with moderate activity. The experimental results in this paper suggest that probably C—H bond activation is not the only route for deactivation of α-diimine palladium catalysts.

To reveal the origin of the high thermal stability for complex **2**, the crystal structure of complex **1b** and complex **2a** was compared with each other. According to Rieger's results [23], the observed N—Pd bond lengths for complex **1b** were 2.004(4) Å and 2.028(4) Å for N1—Pd and N2—Pd, respectively. The C1—C2 bond length was 1.463(7) Å. The C1—N1 bond length was 1.275(6) Å. The C2—N2 bond length was 1.280(6) Å. The N1—Pd—N2 angle was 79.73(15)°. According to these data and the data in Table 1, the schematic diagrams of the five-membered α-diimine ring of complex **1b** and complex **2a** could be deduced and shown in Fig. 3. Each edge of the α-diimine ring of complex **2a** is longer than the corresponding edge of complex **1b**. The framework of complex **2a** is larger than that of complex **1b**. Furthermore, the distance between Pd and C1—C2 bond in complex **2a** (2.778 Å) is longer than that in complex **1b** (2.690 Å). Thus, the Pd atom in complex **2a** experiences less repulsion force from the α-diimine ligand. We propose that this could be the probable reason for the good thermal stability of complex **2a** in the polymerization reaction.

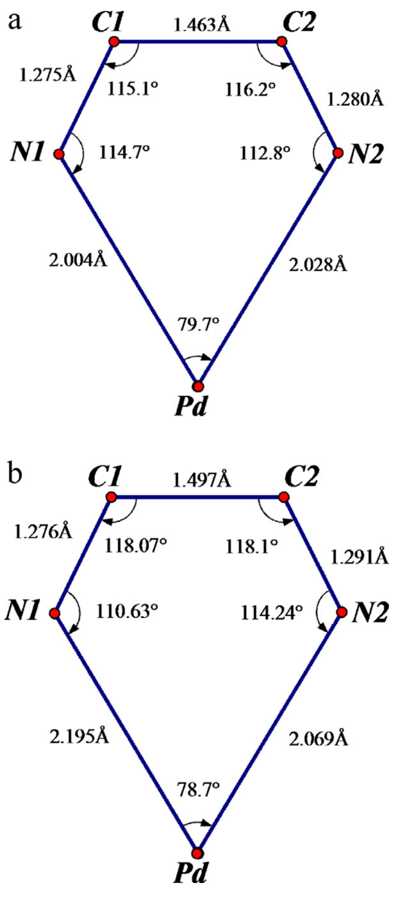

Fig. 3. Schematic diagrams of the five-membered α-diimine ring: (a) complex **1b**; (b) complex **2a**.

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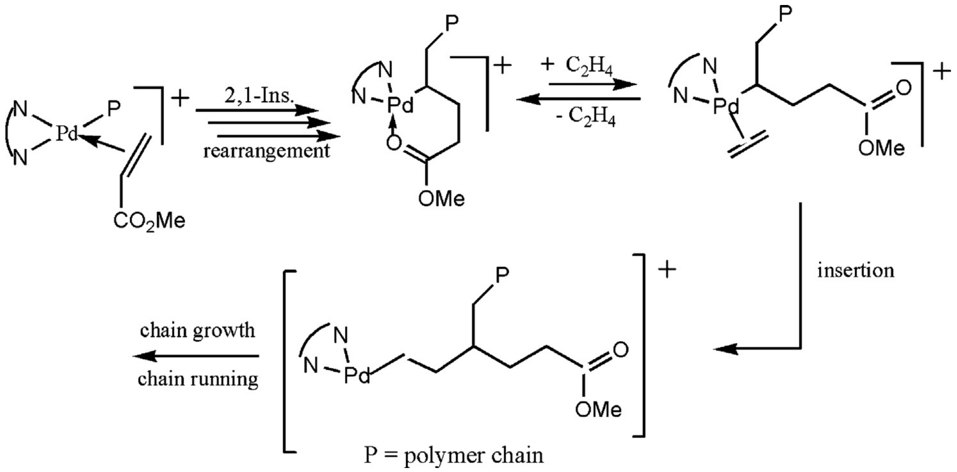
Table 4
Ethylene/methylacrylate copolymerization catalyzed by complex **2**[a].

Entry	Condition	$[MA]_0$[b]	MA%[c]	Acti.[d]	M_{w1}[e]/PDI_1	M_{w2}[e]/PDI_2
1′	**2a**, 25 °C	58	0.84	907	-	1.4/1.5
2′	**2a**, 25 °C	116	1.67	583	3.3/1.3	0.8/1.2
3′	**2a**, 25 °C	174	2.01	151	2.8/1.3	0.7/1.2
4′	**2a**, 50 °C	174	2.45	154	3.9/1.6	0.4/1.2
5′	**2b**, 25 °C	58	1.44	678	5.8/1.2	-
6′	**2b**, 25 °C	116	1.93	319	5.5/1.2	-
7′	**2b**, 25 °C	174	2.11	123	4.8/1.2	-
8′	**2b**, 50 °C	174	4.03	246	4.1/1.2	-

[a] Polymerization condition: 10 μmol complex **2**, 10 μmol cocatalyst ($Li(Et_2O)_{2.8}B(C_6F_5)_4$), 10 mL toluene, 0.1 MPa ethylene.
[b] mmol/L.
[c] Molar percentage.
[d] g/molPd•h.
[e] $\times 10^4$. For some samples (entry 2′–4′) there were two peaks on the GPC curve.



Scheme 4. The mechanistic pathway of ethylene/methyl acrylate copolymerization catalyzed by α-diimine palladium catalyst [9].

4. Conclusions

A thermal stable α-diimine palladium complex for ethylene homopolymerization and ethylene/methylacrylate copolymerization was prepared. The unique structure of the unsymmetrical α-diimine ligand, especially the rigid naphthyl group on the backbone, significantly reduces the push and squeeze of the ligand around Pd atom. Presumably, this suppresses the repulsion force from the α-diimine ligand, thus enhancing the thermal stability of the α-diimine palladium complex. Further mechanistic studies and structural modification of the thermal stable α-diimine palladium complexes are currently under way.

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