Synthesis of palladium complexes containing 2-methoxycarbonyl-6-iminopyridine ligand and their catalytic behaviors in reaction of ethylene and norbornene

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Abstract

A series of palladium complexes (**C1**–**C7**) have been prepared by the reaction of $PdCl_2(CH_3CN)_2$ with 2-methoxycarbonyl-6-imino-pyridines, **L1**–**L7**. The 2-methoxycarbonyl-6-iminopyridines and their complexes were fully characterized by FT-IR, NMR spectra and elemental analysis. Structures of **C1**, **C2**, **C4**, **C5** and **C6**, **C7** were determined by X-ray crystallography, and these complexes fold slightly distorted square planar structures around palladium coordinated with two nitrogen atoms and two chlorides. These palladium complexes exhibited moderate catalytic activities for ethylene dimerization and/or polymerization in the presence of methylaluminoxane, and showed remarkable catalytic activity for norbornene polymerization. The catalytic behaviors of these complexes were highly affected by both the ligand employed and reaction conditions.
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1. Introduction

Olefin polymerization using late transition metal complex catalysts has received great attraction over the past decade especially since the Brookhart's discovery of palladium(II) and nickel(II) complexes containing α-diimine ligands, which exhibited notable catalytic activities for polymerization of ethylene and α-olefins affording high molecular weight polymers with uniform composition [1]. The origin of this success for using these complexes with α-diimine ligand has been postulated that bulky substituents on the ligand hinder the apical coordination sites, leading

to prevention of certain chain-transfer process (β-hydrogen elimination and subsequent dissociation of olefins) [1a,2]. Following this pioneer work, many reports for syntheses and ethylene polymerization/oligomerization using various nickel and palladium complexes containing bidentate nitrogen ligands, such as bipyridine [3] and imino-pyridine ligands [4] were reported as the modified forms. However, in most cases, the nickel complexes showed higher catalytic activities for ethylene polymerization/oligomerization, and their palladium analogues usually showed low catalytic activities [5].

The polymerization of strained cycloalkanes like norbornene using transition metal complex catalysts produced polymers with promising possibilities as high-performance polymeric materials [6] with unique properties such as good
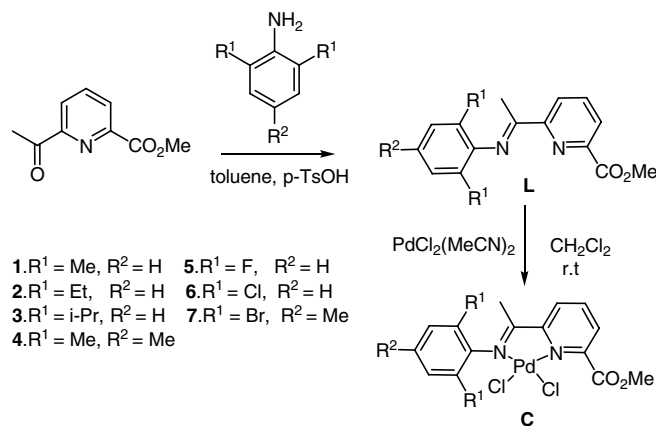
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mechanical strength, optical transparency and low birefrin-gence [7]. Simple palladium(II) salts and their nitrile or phosphine adducts were used as the conventional catalyst precursors for norbornene polymerization [8], but recent rapid progress introduced more efficient palladium com-plex catalysts [9,10] by modification of ligands, the pro-posed cationic catalytically-active species [8,11]. MAO was often used as cocatalyst to activate various palla-dium-based precursors [10,12].

There were numerous reports dealing with late-transi-tion catalytic systems for polynorbornenes, seldom with measuring the molecular weights of polynorbornenes. The polymers without information of molecular weights and distributions would be difficult to explore their proper-ties and find their application. Fortunately, the nickel com-plexes as catalysts for norbornene polymerization not only showed high catalytic activities but also produced the solv-able polynorbornenes with successively measuring their molecular weights and distributions [13], which were earli-est documented with molecular weights of polymers produced by homopolymerization of norbornene [14]. Meanwhile, Novak and Li groups [15] reported that neu-tral palladium complexes are efficient catalytic precursors for olefin and vinyl monomer polymerization although both molecular weights and the distributions for resultant polynorbornenes were not described. The palladium com-plexes containing pyrazolylpyridines were known to be active for ethylene polymerization [16], and most palladium complexes show only moderate activity for either oligomer-ization or polymerization of ethylene [17]. The nickel, cobalt and iron complexes containing 2-ethoxycarbonyl-6-iminopyridines showed unique characteristics in ethylene oligomerization and/or polymerization [18]. It is worthy to try the synthesis and catalytic measurement of their palla-dium analogues. The titled complexes had been synthesized and tested for olefin reactivity. The palladium complexes containing 2-methoxycarbonyl-6-iminopyridines showed moderate activity for ethylene oligomerization as well as polymerization, it is unusual to observe the combined products of oligomer and polymer in palladium catalytic systems. Moreover, their behavior for norbornene poly-merization was investigated to show their high catalytic activity. Herein we describe the synthesis and characteriza-tion of the titled complexes as well as their catalytic behav-iors in ethylene and norbornene reactivity.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization

2-Methoxycarbonyl-6-iminopyridines **L1–L7** shown in Scheme 1 were prepared according to the previous proce-dure [18], by the condensation of methyl 6-acetylpyridine-2-carboxylate with appropriate aniline in the presence of catalytic amount of *p*-TsOH. The palladium (II) dichloride complexes **C1–C7** were thus obtained by the reaction of the corresponding ligands with $PdCl_2(CH_3CN)_2$ in dichloro-

1. R^1 = Me, R^2 = H   **5.** R^1 = F, R^2 = H
2. R^1 = Et, R^2 = H   **6.** R^1 = Cl, R^2 = H
3. R^1 = i-Pr, R^2 = H   **7.** R^1 = Br, R^2 = Me
4. R^1 = Me, R^2 = Me

Scheme 1.

methane at room temperature (Scheme 1). Complexes **C1, C2** and **C5** tended to precipitate from the reaction solution, and optimized yields were obtained when the reaction was continued for a desired period of time. Complexes **C3, C4, C6** and **C7** were precipitated by adding excessive amount of Et_2O. All methyl 2-carboxylate-6-iminopyridines are yel-low solids, while their palladium complexes are orange solids.

All newly synthesized compounds were fully character-ized and confirmed by IR, NMR and elemental analysis. Comparing their IR spectra, we noted that the palladium complexes did not show the suitable absorptions in the C=N range. This observation is attributed to the infrared inactive C=N vibration in the palladium complexes [19], which confirms the coordination of palladium with imino groups. Moreover, the shifts of the NMR peaks of the pal-ladium complexes provide additional evidences for the exis-tence of strong coordination of the pyridine nitrogen and the imine nitrogen to the palladium center [4].

2.2. Structural features

The single crystals of complexes **C1, C2, C4, C5, C6, C7** suitable for X-ray crystallography were grown by diffusing Et_2O into the CH_2Cl_2 solution. Crystallographic data and refinement residuals are summarized in Table 1. The coor-dination geometry around the palladium atom in all title complexes can be described as a distorted square planar. Therefore, the complexes **C1, C5, C6** were discussed here, while their analogues **C2, C4** and **C7** were only collected in the supporting information. The molecular structures of complexes **C1, C5, C6** are depicted in Figs. 1–3, respec-tively, and their selected bond lengths and bond angles are summarized in Table 2. As shown in Table 2, their corre-sponding bond lengths and angles in the coordination pal-ladium frame are similar. Hence, the crystal structures of complexes **C1** and **C5** are selected to be described in detail.

The molecular structure of complex **C1** is shown in Fig. 1. The palladium center is coordinated by two nitrogen and two chlorine atoms, which is different from its nickel

Table 1
Crystallographic data and refinement for complexes **C1**, **C2**, **C4**, **C5**, **C6** and **C7**

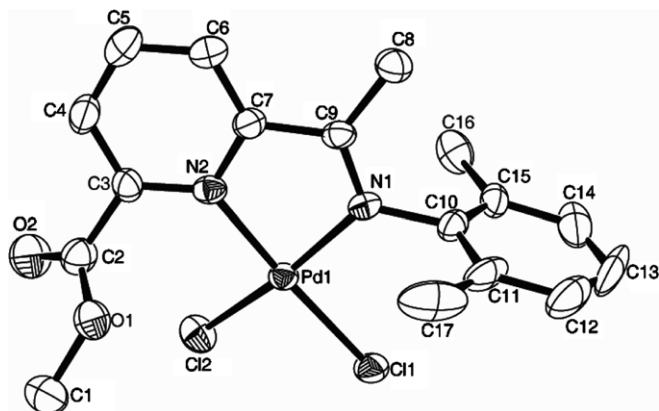|	C1	C2	C4	C5	C6	C7
Empirical formula	$C_{17}H_{18}Cl_2N_2O_2Pd$	$C_{19}H_{22}Cl_2N_2O_2Pd$	$C_{18}H_{20}Cl_2 N_2O_2Pd$	$C_{15}H_{12}Cl_2 F_2N_2O_2Pd$	$C_{15}H_{12}Cl_4$-N_2O_2Pd	$C_{16}H_{14}Br_2Cl_2$-N_2O_2Pd
Formula weight	459.63	487.69	473.66	467.57	500.47	603.41
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pna*2(1)	*P*2(1)/c	*Pna*2(1)	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*n*
Unit cell dimensions						
a (Å)	16.558(3)	13.445(3)	17.212(5)	7.585(3)	7.560(3)	8.866(4)
b (Å)	7.9864(16)	9.4185(19)	7.995(2)	11.738(5)	12.349(5)	8.916(4)
c (Å)	13.439(3)	17.195(3)	13.392 (4)	18.494(8)	19.201(9)	24.463(11)
α (°)	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	90.00	105.36(3)	90.00	99.623(7)	99.662(6)	99.684(4)
γ (°)	90.00	90.00	90.00	90.00	90.00	90.00
V (Å³)	1777.1(6)	2099.7(7)	1842.8(10)	1623.4(12)	1767.0(13)	1906.2(14)
Z	4	4	4	4	4	4
d_{calc} (g cm⁻³)	1.718	1.543	1.707	1.913	1.881	2.103
θ Range (°)	2.83–27.47	1.57– 27.48	2.37–27.48	3.23–27.46	2.15–25.02	3.10–27.48
Number of data collected	2129	4709	4184	3691	3110	4370
Number of parameters refined	217	223	226	217	217	226
Number of unique data	1637	3229	4085	3504	2775	4047
R	0.0365	0.0427	0.0249	0.0204	0.0496	0.0260
R_w	0.0748	0.1111	0.0571	0.0488	0.0797	0.0590
Goodness-of-fit	0.908	0.990	1.062	1.069	1.195	1.082

Fig. 1. Molecular structure of complex **C1**. Hydrogen atoms are omitted for clarity.
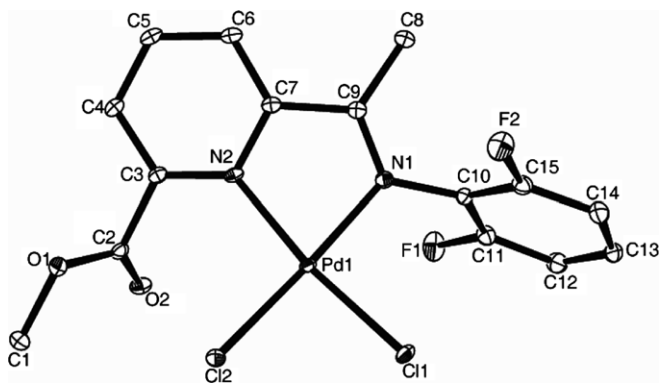

Fig. 2. Molecular structure of complex **C5**. Hydrogen atoms are omitted for clarity.
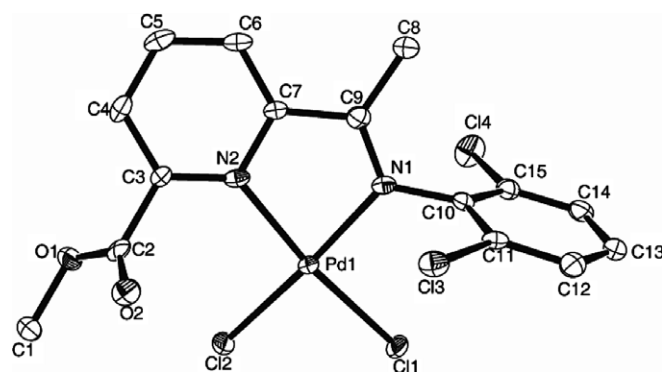

Fig. 3. Molecular structure of **C6**. Hydrogen atoms are omitted for clarity.

analogue coordinated by two nitrogen and oxygen atoms along with two chlorides [18a]. There is no direct bonding between palladium and oxygen atoms such as O1···Pd1 (3.397 Å) and O2···Pd1 (4.354 Å). The average deviation from the plane of Pd1–N2–C7–C9–N1 is 0.1142 Å, which indicates that the coordination is nearly the plane. According to the literature [20], the Pd–Cl distances in **C1** (2.314 (2) Å) and (2.2783 (19) Å) are within the normal range of Pd–Cl bonds, and the Pd–N bonds were measured as Pd–N(py) (2.023(6) Å) and Pd–N(imino) (2.014(5) Å).

The bond angle of N1–Pd–N2 (79.4(2)°) results from the relatively longer Pd–N bonds than other C–N and C–C bonds in the coordination plane. Therefore, the palladium complexes display the distorted planar structure. The structural feature of the distorted square was often observed in other palladium complexes ligated by pyridylimine or bipyridine [21]. The plane of the phenyl ring is oriented

Table 2
Selected bond lengths and bond angles for complexes **C1**, **C5**, and **C6**

	Bond length (Å)			Bond angle(°)	
C1	Pd(1)–N(1)	2.014(5)	Pd(1)–Cl(1)	2.2784(19)	N(1)–Pd(1)–N(2)	79.4(2)
	Pd(1)–N(2)	2.023(6)	Pd(1)–Cl(2)	2.314(2)	Cl(1)–Pd(1)–Cl(2)	87.39(8)
	N(2)–C(7)	1.353(9)	N(2)–C(3)	1.362(9)	N(2)–Pd(1)–Cl(2)	98.52(18)
	N(1)–C(9)	1.289(9)	N(1)–C(10)	1.480(8)	N(1)–Pd(1)–Cl(1)	95.30(18)
C5	Pd(1)–N(1)	2.0217(15)	Pd(1)–Cl(1)	2.2723(8)	N(1)–Pd(1)–N(2)	79.17(6)
	Pd(1)–N(2)	2.0607(16)	Pd(1)–Cl(2)	2.2863(8)	Cl(1)–Pd(1)–Cl(2)	93.27(5)
	N(2)–C(7)	1.373(2)	N(1)–C(10)	1.430(2)	N(1)–Pd(1)–Cl(1)	93.27(5)
	N(1)–C(9)	1.293(2)	N(2)–C(3)	1.332(2)	N(2)–Pd(1)–Cl(2)	99.00(5)
C6	Pd(1)–N(1)	2.019(4)	Pd(1)–Cl(1)	2.2752(15)	N(1)–Pd(1)–N(2)	79.47(17)
	Pd(1)–N(2)	2.069(4)	Pd(1)–Cl(2)	2.2857(15)	Cl(1)–Pd(1)–Cl(2)	88.96(5)
	N(2)–C(7)	1.387(6)	N(1)–C(10)	1.432(7)	N(1)–Pd(1)–Cl(1)	93.10(13)
	N(1)–C(9)	1.283(7)	N(2)–C(3)	1.336(6)	N(2)–Pd(1)–Cl(2)	98.30(12)

approximately orthogonal to the coordination plane with the angle of 92.6°.

For **C5**, the average deviation from the plane of Pd1, N1, C9, C7, N2 is 0.0991 Å, and the dihedral angle between the coordination plane and phenyl ring is 74.5°. There is no direct interaction between palladium and oxygen atom (O2) with the distance of 3.574 Å, but the distance is much shorter than that (4.354 Å) of **C1**. The plausible explanation for this observation is the influence of ligand containing electron-withdrawing fluoro-group that decreased the electron density on N atom of the imine, which in turn decreased electron density on metal atom resulting in a weak interaction between electron donating oxygen and palladium atom.

For **C6**, the average deviation from the coordination plane of Pd1, N1, C9, C7, N2 is 0.0896 Å, and the dihedral angle between the coordination plane and phenyl ring is 76.0°. The bond lengths of Pd–N1 and Pd–N2 are nearly the same with that of **C5**, the distance of Pd–O2 (3.615 Å) indicates the weak interaction between palladium and oxygen atom (O2).

2.3. Ethylene reaction

The catalytic activities of precursors **C1**–**C7** for ethylene dimerization and polymerization were determined in the presence of methylaluminoxane (MAO) as cocatalyst. At ambient pressure, these complexes were inactive for ethylene reaction. By increasing the ethylene pressure to 8 atm, polyethylene was obtained along with butene without other oligomers, which is the first example of simultaneous dimerization and polymerization of ethylene by catalytic system of palladium complexes. The results of ethylene dimerization and polymerization are listed in Table 3.

The results show that the ligand environment had significant influence on ethylene reactivity. There are two types of substituents on the aryl group of imine, the alkyl and halide. As shown in the entries 1–3 of Table 3, the dimerization activity decrease in the order **C1** > **C2** > **C3**. For ethylene polymerization, the activity decrease in the order **C3** > **C2** > **C1**, which is consistent with the fact that catalytic activity increases along with their bulky effects. For the complexes that incorporated halides, the activity decreases in the order **C5** > **C6** > **C7**. Those observations reveal that the less bulky substituents will ease ethylene coordination on active centers and lead higher ethylene reactivity [22].

Two individual active sites are possibly formed as the catalytic centers in the catalytic systems, one which catalyzes the dimerization of ethylene for butene, and the other which polymerizes ethylene to polymer. Due to the equipments limits, those active sites could not be determined yet.

Table 3
Ethylene reaction catalyzed by palladium complexes with MAO

Entry number	Precursor	Al/Pd	Production activity[c]	Dimerization (g)	Polyethylene (g)	T_m (°C)
1	**C1**	1000	8.84	0.418	0.024	130.7
2	**C2**	1000	6.14	0.272	0.035	133.5
3	**C3**	1000	6.80	0.300	0.040	134.0
4	**C4**	1000	12.3	0.570	0.045	134.1
5	**C5**	1000	8.86	0.402	0.041	133.5
6	**C6**	1000	7.86	0.361	0.032	132.8
7	**C7**	1000	3.44	0.151	0.021	nd
8	**C4**	500	3.60	0.170	0.010	nd
9[a]	**C4**	1000	5.64	0.267	0.015	133.2
10[b]	**C4**	1000	15.0	0.750	Trace	nd

Reaction conditions: 5 μmol complex, 150 mL toluene, 8 atm ethylene, 1 h, 20 °C.
[a] Adding Ph_3P with ratio of $Pd/Ph_3P = 1:2$.
[b] Solvent: CH_2Cl_2.
[c] 10^4 g PE/molPd h.

However, some additional experiments of precursor **C4** were performed to confirm the formation of different catalytic centers. Changing the ratio of MAO to palladium (entry 8) does not change the ratio of active centers except for lowering the activities. Adding auxiliary ligand of Ph₃P (entry 9) to the reactor, the catalytic activities of both ethylene dimerization and polymerization decreased because of the potential coordination of auxiliary ligands with active sites [23]. Changing the solvent by using dichloromethane (entry 10), higher activity of ethylene dimerization was obtained. Therefore, one major active site was possibly formed to perform ethylene dimerization. In this case, the catalytic sites might be selectively formed because of solvent environment. Due to the low catalytic activity of ethylene polymerization, the T_m of polyethylene obtained were measured and ranged from 130.7 to 134 °C, which are in line with the characteristics of HDPE.

2.4. Polymerization of norbornene

The palladium complexes were further investigated for catalyzing the vinyl-polymerization of norbornene. Preliminary experiments demonstrated that the single-component palladium complex does not polymerize norbornene. However, when MAO was used as the co-catalyst, the title palladium complexes displayed high activities for norbornene polymerization. The results of vinyl-polymerization of norbornene are summarized in Table 4. In general, the complexes containing the ligand with electron- withdrawing halides exhibit higher catalytic activities than those of other complexes, and the order is **C5** > **C6** > **C7** > **C1** > **C2** > **C3** > **C4**. The **C5** and **C1** showed better activity for complexes incorporating the halides or alky groups individually. It is worth noting that both the size of the difluro and methyl substituents are smaller than that of other halides and other alkyl groups, which can explain for it. In addition to the electronic effect, less bulky substituents provide the favorable environmental insertion of norbornene, and therefore, result in higher catalytic activity. This result is in contrast with what has been observed for some nickel catalytic systems [24], for which no clear effect of stereo-bulky of substitutes on the catalytic activities was observed.

As usual, various reaction parameters, including monomer concentration, the ratio of Al/Pd, reaction tempera-

ture and the reaction time, were probed for their effects on catalytic activities and polymer yields. Like in nickel systems studied previously [13], a significant improvement of catalytic activity was observed when either molar ratio of MAO to the palladium precursor or the concentration of norbornene was increased. It has been noted that longer reaction time rendered higher yield of polymers, and the activity of the catalyst decreased rapidly due to the presence of less number of monomers in the system. The optimal temperature is between 15 and 25 °C for individual palladium precursors in the norbornene polymerization. Unlike the poly(norbornene) obtained in nickel catalytic systems [13], the poly(norbornene) generated from palladium catalytic systems could not be measured for their molecular weights and distributions, partly because it was not fully soluble in diclorobenzene. This may be the reason that molecular weight information of poly(norbornene) was often not reported until our report on nickel catalytic system [13]. The poly(norbornene) obtained in palladium systems produce some polymers with high molecular weight which is beyond the measurement scale of GPC. Moreover, the absence of the peaks corresponding to C=C double bond in IR spectra indicates the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization (ROMP) [25,13].

3. Conclusions

A series of palladium complexes containing 2-methoxycarbonyl-6-iminopyridine ligands have been synthesized and characterized along with their single-crystal X-ray analysis. Activated with MAO, they showed moderate activity for ethylene dimerization and polymerization simultaneously. There are two different catalytically active sites for ethylene dimerization and polymerization, individually. The productivity increased with the decrease of bulky substituents, because the less bulky substituents will ease ethylene coordination on the active center and give higher ethylene reactivity. Though good catalytic activities were obtained for vinyl-polymerization of norbornene, the PNB is less interesting because of their partly insolubility. These new palladium catalysts exhibit interesting properties for ethylene and norbornene reactivity, and the reaction conditions greatly affect the products.

4. Experimental section

4.1. General procedures

All manipulations of the moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Melting points were determined with a digital electrothermal apparatus without calibration. The IR spectra were obtained on a Perkin–Elmer FT-IR 2000 spectrophotometer by using the KBr disc in the range of 4000–400 cm⁻¹. The NMR spectra were recorded on a Bruker DMX-300 instrument with TMS as

Table 4
Norbornene polymerization

Entry	Precursor	Activity (10^5 gPNB mol⁻¹Pd h⁻¹)	Yield (%)
1	**C1**	8.23	58.4
2	**C2**	8.05	57.1
3	**C3**	8.00	56.7
4	**C4**	7.92	56.2
5	**C5**	10.5	74.5
6	**C6**	10.0	71.1
7	**C7**	8.57	61.4

Reaction conditions: 5 μmol complex, total volume 30 mL with toluene as solvent [norbornene]/[Pd] = 5000, MAO/Pd = 1000, 20 °C, 30 min.

the internal standard. Elemental analyses were performed on a Flash EA 1112 microanalyzer.

Melting points of the polymers were obtained on a Perkin–Elmer DSC-7 in the standard DSC run mode. The instrument was initially calibrated for melting point of an indium standard at a heating rate of 10 °C/min. The polymer sample was first equilibrated at 0 °C and then heated to 160 °C at a rate of 10 °C/min to remove thermal history. The sample was then cooled to 0 °C at a rate of 10 °C/min. A second heating cycle was used for collecting DSC thermo gram data at a ramping rate of 10 °C/min. Toluene was refluxed over sodium–benzophenone until the purple color appeared and distilled under nitrogen prior to use. Dichloride methane was distilled under nitrogen from CaH$_2$. All other chemicals were obtained commercially and used without further purification unless stated otherwise.

4.2. Synthesis of palladium complexes

4.2.1. Synthesis of 2-methoxycarbonyl-6-iminopyridine

The compound was prepared according to the literature method [18], except that ethyl acetate and ethanol were used, instead of methyl acetate and methanol. The desired compound 2-methoxycarbonyl-6-acetylpyridine, was obtained as white solid in 30.0% yield after purified by column chromatography (silica-gel, petroleum ether:ethyl acetate = 8:1); m.p.: 64 °C. IR (Nujol, cm^{-1}): 1721 (COOCH$_3$); 1700 (C=O).^{1}H NMR (CDCl$_3$): δ 8.27 (d, 1H, $J = 6.51$ Hz, Py–H); 8.21 (d, 1H, $J = 6.51$ Hz, Py–H); 8.01 (t, 1H, $J = 7.89$ Hz, Py–H); 4.04 (s, 3H, –OCH$_3$); 2.81 (s, 3H, C(O)CH$_3$). ^{13}C NMR (CDCl$_3$): δ 199.8, 165.4, 153.8, 147.8, 138.2, 128.4, 124.8, 53.2, 25.9. Anal. Calc. for C$_9$H$_9$NO$_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.10; H, 4.95; N, 7.81%.

4.2.2. Synthesis of 2-methoxycarbonyl-6-(1-(2,6-dimethylphenylimino)ethyl)pyridyl palladium dichloride (C1)

All synthesis of L1–L7 and C1–C7 were prepared by similar procedures, thus only the synthesis of L1 and C1 is described in detail. A solution of 2-methoxycarbonyl-6-acetylpyridine (0.500 g, 3.3 mmol) and 2,6-dimethylaniline (0.500 g, 4.26 mmol), and p-toluenesulfonic acid (0.05 g) with 4 Å molecular sieves in toluene (50 mL) was refluxed for 12 h. The mixture was cooled to room temperature, filtered, and separated by column chromatography (silica-gel, petroleum ether: EtOAc = 15:1). The product, 2-methoxycarbonyl-6-(1-(2,6-dimethylphenylimino)ethyl)pyridine (L1), was obtained as yellow crystals (0.726 g, 2.6 mmol) in yield 92.2%; m.p.: 100 °C; IR (Nujol, cm^{-1}): 1718 (COOCH$_3$), 1646 (C=N). ^{1}H NMR(CDCl$_3$): δ 8.60 (d, 1H, $J = 7.26$ Hz, Py–H), 8.22 (d, 1H, $J = 7.56$ Hz, Py–H), 7.93 (t, 1H, $J = 7.28$ Hz, Py–H), 7.06 (d, 2H, $J = 7.60$ Hz, Ar–H), 6.95 (t, 1H, $J = 6.78$ Hz, Ar–H), 4.05 (s, 3H, –OCH$_3$), 2.25 (s, 3H, C(CH$_3$)=N), 2.02 (s, 6H, –CH$_3$). ^{13}C NMR (CDCl$_3$): δ 167.0, 165.8, 156.5, 148.6, 147.2, 137.5, 128.0, 126.4, 125.4, 124.6, 123.3, 53.0, 18.0, 16.6. Anal. Calc. for C$_{17}$H$_{18}$N$_2$O$_2$: C, 72.32; N, 9.92; H, 6.43. Found: C, 72.10; N, 9.64; H, 6.49%.

To ligand L1 (0.2821 g, 1 mmol) and PdCl$_2$(CH$_3$CN)$_2$ (0.259 g, 1 mmol) was added 10 mL fresh distilled dichloromethane at the room temperature .The reaction mixture was stirred 24 h, and 10 mL diethyl ether was added to precipitate the complex. The desired complex, 2-methoxycarbonyl-6-(1-(2,6-dimethylphenylimino)ethyl)pyridyl palladium dichloride (C1), was obtained as orange powder (0.413 g) in 89.7% yield. IR (Nujol, cm^{-1}): 1743; 1589. ^{1}H NMR (CD$_3$OCD$_3$): δ 8.58 (t, 1H, $J = 9.00$ Hz, Py–H), 8.49 (d, 1H, $J = 6.00$ Hz, Py–H), 8.04 (d, 1H, $J = 6.00$ Hz, Py–H), 7.12 (m, 3H, Ar–H), 3.89 (s, 3H, OCH$_3$), 2.41 (s, 3H, CH$_3$C=N), 2.27 (s, 6H, CH$_3$). ^{13}C NMR(d_6-DMSO): δ 167.1, 165.4, 156.2, 148.8, 147.2, 138.9, 128.9, 128.3, 126.9, 125.2, 124.9, 123.5, 53.1, 18.6, 18.0. Anal. Calc. for C$_{17}$H$_{18}$Cl$_2$N$_2$O$_2$Pd: C, 44.42; H, 3.95; N, 6.09. Found: C, 44.28; H, 4.16; N, 6.09%.

4.2.3. Synthesis of 2-methoxycarbonyl-6-(1-(2,6-diethylphenylimino)ethyl)pyridyl palladium dichloride (C2)

Using the same procedure for L1, by 2-methoxycarbonyl-6-acetylpyridine (0.500 g, 3.3 mmol) and 2, 6-diethylaniline (0.520 g, 3.50 mmol), the 2-methoxycarbonyl-6-(1-(2,6-diethylphenylimino)ethyl)pyridine (L2) was obtained as yellow powder (0.705 g, 2.27 mmol) in yield 68.8%; m.p.: 98 °C; IR (Nujol, cm^{-1}): 1728 (COOCH$_3$), 1637 (C=N). ^{1}H NMR (CDCl$_3$): δ 8.57 (d, 1H, $J = 7.23$ Hz, Py–H), 8.21(d, 1H, $J = 7.56$ Hz, Py–H), 7.94 (t, 1H, $J = 7.92$ Hz, Py–H), 7.12 (d, 2H, $J = 6.51$ Hz, Ar–H), 7.03 (t, 1H, $J = 6.74$ Hz, Ar–H), 4.02 (s, 3H, –OCH$_3$), 2.36 (m, 4H, $J = 9.27$ Hz, CH$_2$-), 2.27(s, 3H, CH$_3$C=N), 1.12(t, 6H, $J = 7.20$ Hz, –CH$_3$). ^{13}C NMR (CDCl$_3$): δ 166.7, 165.8, 156.5, 147.6, 147.2, 137.5, 131.1, 126.3, 126.0, 124.5, 123.6, 52.9, 24.7, 16.9, 13.8. Anal. Calc. for C$_{19}$H$_{22}$N$_2$O$_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.60; H, 7.14; N, 9.03%. Using ligand L2 (0.310 g, 1 mmol) and PdCl$_2$(CH$_3$CN)$_2$ (0.259 g, 1 mmol), the 2-methoxycarbonyl-6-(1-(2,6-diethylphenylimino)ethyl)pyridyl palladium dichloride (C2)(0.442 g, 0.91 mmol) was obtained in 91.0% yield. IR (Nujol, cm^{-1}): 1738(COOCH$_3$), 1589(C=N). ^{1}H NMR (CDCl$_3$): δ 8.37 (t, 1H, $J = 7.89$ Hz, Py–H), 8.10 (d, 1H, $J = 6.54$ Hz, Py–H), 8.01 (d, 1H, $J = 6.54$ Hz, Py–H), 7.31 (t, 1H, $J = 6.87$ Hz, Ar–H), 7.18 (d, 2H, $J = 7.56$ Hz, Ar–H), 4.02 (s, 3H, –OCH$_3$), 2.84 (m, 2H, –CH$_2$-), 2.48 (d, 2H, $J = 7.56$ Hz, –CH$_2$-), 2.25 (s, 3H, CH$_3$C=N), 1.31 (t, 6H, $J = 7.56$ Hz, –CH$_3$). Anal. Calc. for C$_{19}$H$_{22}$Cl$_2$N$_2$O$_2$Pd: C, 46.79; H, 4.55; N, 5.74. Found: C, 46.62; H, 4.55; N, 5.73. ^{13}C NMR(CDCl$_3$): δ 167.0, 165.4, 156.0, 147.8, 139.1, 126.9, 126.2, 124.8, 123.9, 53.1, 24.7, 17.2, 14.4%.

4.2.4. Synthesis of 2-methoxycarbonyl-6-(1-(2,6-di-i-propylphenylimino)ethyl)pyridyl palladium dichloride (C3)

Using the same procedure for L1, by 2-methoxycarbonyl-6-acetylpyridine (0.500 g, 3.3 mmol) and 2,6-dipro-

pylaniline (1.20 g, 3.55 mmol), the 2-methoxycarbonyl-6-(1-(2,6-di-*i*-propylphenylimino)ethyl)pyridine (**L3**) was obtained as yellow crystals (0.507 g, 1.50 mmol) in 45.4% yield; m.p.: 148–150 °C. IR (Nujol, cm^{-1}): 1725(COOCH$_3$), 1648(C=N). ^{1}H NMR (CDCl$_3$): δ 8.59 (d, 1H, $J = 6.87$ Hz, Py–H); 8.21 (d, 1H, $J = 7.05$ Hz, Py–H), 7.95 (t, 1H, $J = 7.89$ Hz, Py–H), 7.16(d, 2H, $J = 6.18$ Hz, Ar–H), 7.12 (t, 1H, Ar–H), 4.02 (s, 3H, OCH$_3$), 2.71 (m, 2H, –CH (CH$_3$)$_2$), 2.28 (s, 3H, CH$_3$C=N), 1.13 (d, 12H, -CH$_3$). ^{13}C NMR (CDCl$_3$): δ 166.6, 165.8, 156.5, 147.2, 146.3, 137.5, 135.7, 126.3, 124.6, 123.8, 123.1, 53.0, 28.3, 23.3, 22.9, 17.2. Anal. Calc. for C$_{21}$H$_{26}$N$_2$O$_2$: C, 74.52; H, 7.74; N, 5.43. Found: C, 74.08; H, 7.74; N, 5.43%. Using ligand **L3** (0.338 g, 1 mmol) and PdCl$_2$(CH$_3$CN)$_2$ (0.259 g, 1 mmol), the 2-methoxycarbonyl-6-(1-(2,6-di-*i*-propylphenylimino) ethyl)pyridyl palladium dichloride (**C3**) (0.289 g, 0.56 mmol) was also obtained in 55.7% yield. IR (Nujol, cm^{-1}): 1733 (COOCH$_3$); 1584. ^{1}H NMR (CDCl$_3$): δ 8.34 (t, 1H, $J = 7.86$ Hz, Py–H), 8.01 (t, 2H, $J = 7.20$ Hz, Py–H), 7.35 (t, 1H, $J = 7.85$ Hz, Ar–H), 7.22 (d, 2H, $J = 7.56$ Hz, Ar–H), 4.03 (s, 3H, –OCH$_3$), 3.10 (m, 2H, –CH(CH$_3$)$_2$), 2.28 (s, 3H, CH$_3$C=N), 1.45 (d, 6H, J = 6.51 Hz, –CH$_3$), 1.14 (d, 6H, $J = 6.87$ Hz, –CH$_3$). ^{13}C NMR(d_6-DMSO): δ 167.1, 165.5, 157.3, 156.0, 147.4, 146.2, 140.3, 139.1, 135.5, 127, 124.7, 124.3, 123.5, 53.1, 28.3, 24.3, 24.2, 23.6, 23.1, 17.5. Anal. Calc. for C$_{21}$H$_{26}$Cl$_2$N$_2$O$_2$Pd: C, 48.90; H, 5.08; N, 5.43. Found: C, 48.57; H, 5.08; N, 5.32%.

4.2.5. Synthesis of 2-methoxycarbonyl-6-(1-(2,4,6-trimethylphenylimino)ethyl)pyridyl palladium dichloride (C4)

Using the same procedure for **L1**, 2-methoxycarbonyl-6-acetylpyridine (0.500 g, 3.3 mmol) and 2,4,6-trimethylaniline (0.490 g, 3.63 mmol), the 2-methoxycarbonyl-6-(1-(2,4,6-trimethylphenylimino) ethyl)pyridine (**L4**) (0.612 g, 2.07 mmol) was obtained as pale yellow solid in yield 62.8%; m.p.: 127 °C. IR (Nujol, cm^{-1}): 1717 (COOCH$_3$), 1634 (C=N). ^{1}H NMR (CDCl$_3$): δ 8.56 (d, 1H, $J = 6.00$ Hz, Py–H), 8.19 (d, 1H, $J = 9.00$ Hz, Py–H), 7.94 (t, 1H, $J = 9.00$ Hz, Py–H), 6.89 (s, 2H, Ar–H), 4.02 (s, 3H, OCH$_3$), 2.29 (s, 3H, CH$_3$C=N), 2.25 (s, 3H, *p*-Ar-CH$_3$), 1.98 (s, 6H, *o*-Ar-CH$_3$). ^{13}C NMR (CDCl$_3$): δ 166.8, 165.6, 156.4, 153.3, 147.2, 146.6, 137.2, 135.6, 129.8, 127.9, 126.9, 126.1, 124.5, 52.9, 21.0, 19.1, 18.7, 17.5. Anal. Calc. for C$_{18}$H$_{20}$N$_2$O$_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.30; H, 6.90; N, 9.45%. Using ligand **L4** (0.296 g, 1 mmol) and PdCl$_2$(CH$_3$CN)$_2$ (0.259 g, 1 mmol), the 2-methoxycarbonyl-6-(1-(2,4,6-trimethylphenylimino)ethyl)-pyridyl palladium dichloride (**C4**) (0.428 g, 0.88 mmol) was also obtained in yield 88.4%. IR (Nujol: cm^{-1}): 1740 (COOCH$_3$), 1587. ^{1}H NMR(CDCl$_3$): δ 8.31 (t, 1H, $J = 6.00$ Hz, Py–H); 8.00 (t, 2H, $J = 6.00$ Hz, Py–H); 6.93 (s, 2H, Ar–H), 4.03 (s, 3H, OCH$_3$), 2.29 (s, 3H, N=C–CH3), 2.26 (s, 6H, *o*-Ar–H), 2.24 (s, 3H, *p*-Ar–H). ^{13}C NMR(d_6-DMSO): δ 167.4, 165.3, 156.3, 153.3, 147.3, 146.4, 139.7, 138.9, 132.1, 130.1, 128.9, 126.9, 125.0, 53.1,

20.9, 19.9, 18.6, 18.0. Anal. Calc. for C$_{21}$H$_{26}$Cl$_2$N$_2$O$_2$Pd · CH$_2$Cl$_2$: C, 40.85; H, 3.97; N, 5.01. Found: C, 40.66; H, 3.97; N, 5.08%.

4.2.6. Synthesis of 2-methoxycarbonyl-6-(1-(2,6-difluorophenylimino)ethyl)pyridyl palladium dichloride (C5)

Using the same procedure for **L1**, 2-methoxycarbonyl-6-acetylpyridine (0.500 g, 3.3 mmol) and 2,6-difuluroaniline (0.500 g, 3.87 mmol), the 2-methoxycarbonyl-6-(1-(2,6-difluorophenylimino)ethyl)pyridine (**L5**) (0.612 g, 2.11 mmol) was obtained as pale yellow solid in yield 64.0%; m.p.: 52 °C. IR (Nujol, cm^{-1}): 1724 (COOCH$_3$); 1649 (C=N). ^{1}H NMR (CDCl$_3$): δ 8.52 (d, 1H, $J = 9.2$ Hz, Py–H), 8.21(d, 1H, $J = 9.2$ Hz, Py–H), 7.94 (t, 1H, $J = 7.84$ Hz, Py–H), 7.03 (m, 1H, Ar–H), 6.97 (m, 2H, Ar–H), 4.02 (s, 3H, OCH$_3$), 2.45 (s, 3H, N=CCH$_3$). ^{13}C NMR (CDCl$_3$): δ 172.4, 165.6, 156.0, 154.6, 154.5, 151.3, 151.2, 147.1, 137.6, 126.7, 125.2, 124.3, 124.2, 111.9, 111.7, 111.5, 52.9, 17.7. Anal. Calc. for C$_{15}$H$_{12}$F$_2$N$_2$O$_2$: C, 62.07; H, 4.17; N, 9.65. Found: C, 62.09; H, 4.29; N, 9.51%. Using ligand **L5** (0.290 g, 1 mmol) and PdCl$_2$(CH$_3$CN)$_2$ (0.259 g, 1 mmol), the 2-methoxycarbonyl-6-(1-(2,6-difluorophenylimino)ethyl)pyridyl palladium dichloride (**C5**)(0.312 g, 0.67 mmol) was obtained in yield 67.0%. IR (Nujol, cm^{-1}): 1732 (COOCH3), 1693 (C=N), 1591. ^{1}H NMR (DMSO): δ 8.26 (t, 1H, $J = 7.24$ Hz, Py–H), 8.20 (m, 2H, Py–H), 6.85 (t, 2H, $J = 6.96$ Hz, Ar–H), 6.50 (m, 1H, Ar–H), 3.90 (s, 3H, OCH$_3$), 2.63 (s, 3H, N=C–CH3). ^{13}C NMR(d_6-DMSO): δ 172.6, 165.3, 155.3, 154.2, 150.9, 147.5, 139.2, 128.8, 127.5, 125.2, 124.9, 112.7, 112.4, 111.1, 53.1, 17.98. Anal. Calc. for C$_{15}$H$_{12}$F$_2$N$_2$O$_2$Pd: C, 38.53; H, 2.59; N, 5.99. Found: C, 37.99; H, 2.53; N, 5.72%.

4.2.7. Synthesis of 2-methoxycarbonyl-6-(1-(2,6-dichlorophenylimino)ethyl)pyridyl palladium dichloride (C6)

Using the same procedure for **L1**, 2-methoxycarbonyl-6-acetylpyridine (0.500 g, 3.3 mmol) and 2,6-dichloroaniline (5.60 g, 3.47 mmol), the 2-methoxycarbonyl-6-(1-(2,6-dichlorophenylimino) ethyl)pyridine (**L6**) (0.274 g, 0.85 mmol) was obtained as pale yellow solid in yield 25.8%. IR: 2954, 1728 (C=O), 1654 (C=N), 1438, 1138, 788, 766. ^{1}H NMR (CDCl$_3$): δ 8.58 (d, 1H, $J = 7.89$ Hz, Py–H), 8.22 (d, 1H, $J = 7.89$ Hz, Py–H), 7.97 (m, 1H, Py–H), 7.36 (m, 2H, $J_1 = 7.89$ Hz, $J_2 = 2.40$ Hz, Ar–H), 7.00 (m, 1H, Ar–H), 4.03(s, 3H, OCH$_3$), 2.38(s, 3H, CH$_3$C=N).^{13}C NMR (CDCl$_3$): δ 172.1, 165.3, 155.5, 147.3, 146.3, 145.5, 137.6, 128.5, 126.7, 125.8, 124.5, 124.4, 52.9, 17.60. Anal. Calc. for C$_{15}$H$_{12}$Cl$_2$N$_2$O$_2$: C, 55.75; H, 3.74; N, 8.67. Found: C, 55.80; H, 3.82; N, 8.20%. Using ligand **L6** (0.323 g, 1 mmol) and PdCl$_2$(CH$_3$CN)$_2$ (0.2590 g, 1 mmol), the 2-methoxycarbonyl-6-(1-(2,6-dichlorophenylimino)ethyl)pyridyl palladium dichloride (**C6**) (0.434 g, 0.87 mmol) was also obtained in yield 87.0%. IR (Nujol, cm^{-1}): 1731 (COOCH3), 1590. ^{1}H NMR (DMSO): δ 8.25 (t, 1H,

$J = 6.00$ Hz, Py–H), 8.20 (m, 2H, Py–H), 7.21 (d, 2H, $J = 6.00$ Hz, Ar–H), 6.58 (t, 1H, $J = 6.52$ Hz, Ar–H), 3.94 (s, 3H, OCH3), 2.29 (s, 3H, N=C–CH3). ^{13}C NMR(d_6-DMSO): δ 172.1, 165.1, 153.4, 147.5, 141.4, 139.6, 129.1, 128.8, 128.5, 124.8, 120.0, 118.6, 117.4, 53.2, 17.9. Anal. Calc. for $C_{21}H_{26}Cl_2N_2O_2Pd$: C, 36.00; H, 2.42; N, 5.60. Found: C, 35.64; H, 2.40; N, 5.39%.

4.2.8. Synthesis of 2-methoxycarbonyl-6-(1-(2,6-dibromo-4-methylphenylimino)ethyl) pyridyl palladium dichloride (C7)

Using the same procedure for **L1**, by 2-methoxycarbonyl-6-acetylpyridine (0.500 g, 3.3 mmol) and 2,6-dibromo-3-methylaniline (0.920 g, 3.50 mmol), the 2-methoxycarbonyl-6-(1-(2,6-dibromo-4-methylphenylimino)ethyl)pyridine (**L7**) (0.351 g, 0.83 mmol) was obtained as pale yellow solid in yield 25.1%; m.p.:124–126 °C. IR (Nujol, cm^{-1}): 1718 (COOCH3); 1635(C=N) .^{1}H NMR (CDCl3): δ 8.58 (d, 1H, $J = 9.00$ Hz, Py–H), 8.22 (d, 1H, $J = 9.00$ Hz, Py–H), 7.96 (t, 1H, $J = 9.00$ Hz, Py–H), 4.03 (s, 3H, OCH3), 2.35 (s, 3H, CH3C=N), 2.32 (s, 3H, o-Ar–CH3). ^{13}C NMR (CDCl3): δ 171.1, 165.6, 155.8, 147.2, 145.3, 137.7, 135.6, 132.6, 126.8, 125.2, 113.0, 52.9, 20.3, 17.6. Anal. Calc. for $C_{16}H_{14}Br_2N_2O_2$: C, 45.10; H, 3.31; N, 6.57. Found: C, 45.89; H, 3.31; N, 6.18%. Using ligand **L7** (0.424 g, 1 mmol) and $PdCl_2(CH_3CN)_2$ (0.259 g, 1.0 mmol), the 2-methoxycarbonyl-6-(1-(2,6-dibromo-4-methylphenylimino)ethyl)-pyridylpalladium dichloride (**C7**) (0.540 g, 0.9 mmol) was obtained in yield 90%. IR (Nujol, cm^{-1}): 1728.35 (COOCH3); 1589, 1613 (C=N).^{1} NMR (DMSO): 8.47 (d, 1H, $J = 6.00$ Hz, Py–H), 8.24(m, 2H, Py–H), 7.58 (s, 2H, $J = 6.05$ Hz, Ar–H), 3.93 (s, 3H, OCH3), 2.31 (s, 3H, N=C–CH3), 2.15 (s, 3H, –CH3). ^{13}C NMR (d_6-DMSO): δ 171.0, 165.3, 155.2, 147.5, 145.1, 139.3, 136.7, 133.0, 127.6, 125.2, 112.9, 53.2, 20.1, 17.8. Anal. Calc. for $C_{16}H_{14}Br_2Cl_2N_2O_2Pd$: C, 31.85; H, 2.34; N, 4.64. Found: C, 31.49; H, 2.45; N, 4.63%.

4.3. General procedure for ethylene polymerization at 1 atm ethylene pressure

A flame dried three-neck round flask was loaded with the complexes **C1**–**C7** and vacuum-filled three times by nitrogen. Then ethylene was charged together with freshly distilled toluene and stirred for 10 min. MAO was added by a syringe. The reaction mixture was stirred under 1 atmospheric ethylene pressure for a limited time, and the catalytic reaction was terminated with acidified water. An aliquot of the reaction mixture was analyzed by GC and GC–MS.

4.4. General procedure for ethylene polymerization at 8 atm ethylene pressure

It was carried out in a 250 ml autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. The desired amount of MAO, 30 ml tolu-ene solution of palladium complex and 120 ml of toluene were added to the reactor in this order under ethylene atmosphere. When being to the reaction temperature, ethylene with the desired pressure (8 atm) was introduced to start the reaction. After 1 h, the reaction was stopped. And then a small amount of the reaction solution was collected, terminated by the addition of 5% aqueous hydrogen chloride and then analyzed by gas chromatography (GC) for determining the distribution of oligomers obtained. Then the residual solution was quenched with HCl–acidified ethanol (5%). The precipitated polymer was collected by filtration, washed with ethanol, dried in vacuum at 60 °C until constant weight, weighed and finally characterized.

4.5. General procedure for polymerization of norbornene

In a typical procedure, the catalyst (5 μmol) was dissolved in a Schlenk tube in 23 ml degassed toluene under nitrogen and a 3.47 ml toluene solution of norbornene (7.20 M, 25 mmol of norbornene) was added via a syringe. The polymerization was initiated by adding 3.57 ml toluene solution of 1.4 mol/L MAO (5.0 mmol). After 30 min, the polymerization was terminated by injecting 200 ml acidic methanol (methanol:HCl(conc.) = 95:5) into the reactor. The polynorbornene was isolated by filtration, washed with methanol, and dried in vacuum at 100 °C for 100 h. The total reaction volume of norbornene polymerization was 30 ml unless otherwise stated, that was achieved by adding solvent when necessary. Similarly, the polymerization of norbornene was also carried out by using toluene as solvent.

4.6. X-ray crystallography measurement

The single-crystal X-ray diffraction for complexes **C1** and **C2** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite monochromated Mo Kα radiation ($λ = 0.71073$ Å) at 120 k and 173 k, respectively. Intensity data of complexes **C4**, **C5**, **C6**, **C7** were collected on a Bruker Smart 1000 CCD diffractometer at 130(2) K with graphite monochromated Mo Kα radiation ($λ = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected. The structures were solved by direct methods and re-fined by full-matrix least-squares on F^2. Each H atom was placed in a calculated position and refined anisotropically. Structure solution and refinement were performed using the SHELXL-97 Package. Crystal data and processing parameters are summarized in Table 1.

Appendix A. Supporting information available

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 291547, 291548, 291549, 291550, 291551 and 291552 for complexes **C1**, **C2**, **C4**, **C5**, **C6** and **C7**, respectively. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam. ac.uk or http://www.ccd.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.026.

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