

Electronic Supporting Information

An extremely high active chiral (S,S)-bis(oxazoline) Pd(II) alkyl complex/activator catalytic system for vinyl polymerization of norbornene in air and water

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Contents

1. **Materials.**
2. **General Methods.**
3. **Synthesis of Complexes 1-6.**
 - 3.1 Synthesis of [R₂-(S, S)-BOZ]Pd(II)Me (R = CH(CH₃)₂) (1).
 - 3.2 Synthesis of [R₂-(S, S)-BOZ]Pd(II)Ph (R = CH(CH₃)₂) (2).
 - 3.3 Synthesis of [R₂-(S, S)-BOZ]Pd(II)Me (R = Ph) (3).
 - 3.4 Synthesis of [R₂-(S, S)-BOZ]Ni(II)Me (R = Ph) (4).
 - 3.5 Synthesis of [R₂-(S, S)-BOZ]Ni(II)Me (R = CH(CH₃)₂) (5).
 - 3.6 Synthesis of [R₂-(S, S)-BOZ]Ni(II)Ph (R = CH(CH₃)₂) (6).
4. **Table S1 Vinyl polymerization of norbornene by chiral Ni alkyl complexes/cocatalyst systems in nitrogen**
5. **Characterization of the palladium complex 1 (C₆D₆) in air for 3 days**
6. **A Typical Procedure for Norbornene (NB) Polymerization by Complex 1/Activator Binary System in Air (Table 2, entry 4).**
7. **A Typical Procedure for Norbornene (NB) Polymerization by Complex 1/Activator Binary System in Air and Water (Table 2, entry 22).**
8. **X-ray Crystallographic Analysis.**
9. **SFigure 1.** IR spectra of PNBs obtained by chiral palladium complexes 1–2/cocatalysts systems under air atmosphere in Table 1 (a: entry 1, b: entry 5).
10. **SFigure 2.** DSC curves of PNBs obtained by the complex 1/activators in Table 1 (a: entry 3, b: entry 24).
11. **SFigure 3.** WAXD diagram of PNBs obtained by chiral palladium methyl complex 1 in Table 1 (a: entry 2)
12. **SFigure 4.** ¹H NMR spectra of PNB.

Reference.

1. **Materials.**

Polymerization performed in air and water were carried out using non-degassed technical grade 1,2-dichlorobenzene (TG-D) from Beijing Weiss Chemical Co., Ltd. without any purification. Water was distilled and non-degassed. Unpretreated

Norbornene without any polymerization inhibitor such as BHT (butylated hydroxytoluene) was purchased from Alfa Aesar and used as received. Anhydrous toluene, THF and hexane from J&K Scientific Ltd. was purified by use of a SPS-800 solvent purification system (Mbraun), and dried over fresh Na chips in the glovebox. Norbornene, chlorobenzene, and 1,2-dichlorobenzene from TCI were dried over CaH₂, vacuum-transferred, and degassed by two freeze-pump-thaw cycles prior to polymerization experiments in nitrogen. [Ph₃C][B(C₆F₅)₄], [PhMe₂NH][B(C₆F₅)₄], and B(C₆F₅)₃ were purchased from Tosoh Finechem Corporation and used without purification. Complexes **1-6** were synthesized under a dry nitrogen atmosphere by use of standard Schlenk techniques or a nitrogen-filled Mbraun glovebox. LiMe and LiPh were purchased from J&K Scientific Ltd. and used without purification. Chiral Pd(II) and Ni(II) chloride complexes [(R₂-(S, S)-BOZ)MCl] (M = Pd(II), Ni(II), R = CH(CH₃)₂, Ph) were synthesized according to the literature.¹ Chiral Ni(II) alkyl complexes (R₂-(S, S)-BOZ)NiR' (**5**, R = CH(CH₃)₂, R' = Me; **6**, R = CH(CH₃)₂, R' = Ph) were synthesized according to the literature.² The deuterated solvents benzene-d₆ (99.6 atom% D) was obtained from Cambridge Isotope.

2. General Methods.

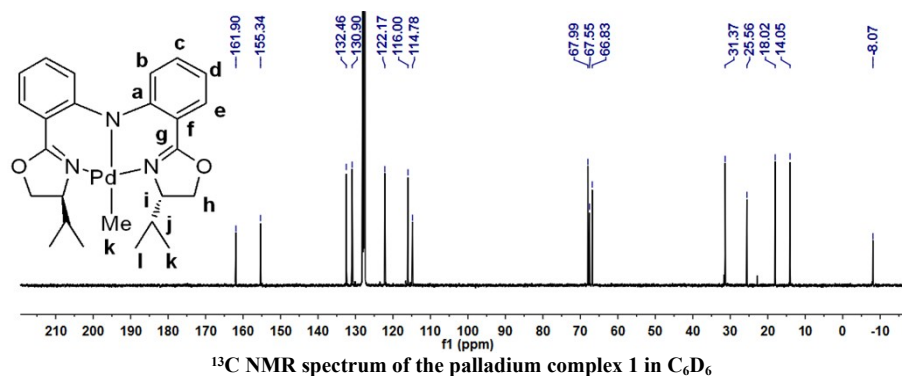
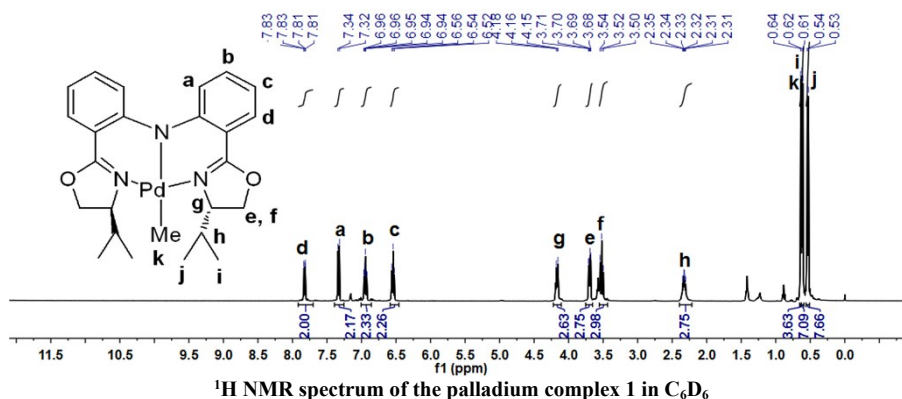
The NMR (¹H, ¹³C) spectra of catalyst precursors were recorded on an AVANCE 400 spectrometer at room temperature with C₆D₆ or as a solvent. All of the resulting polynorbornenes are insoluble in common solvents such as chloroform, hexane, benzene, toluene, chlorobenzene, and accordingly cannot be characterized by NMR and GPC methods. The DSC measurements were performed on a TA60 (TA Co.) at a rate of 10 °C/min from 30 °C to 550 °C. The WAXD diagram of the polymer powder was obtained by using of a Bruker-AXS X-ray diffractometer with monochromatic radiation at a wavelength of 0.154 nm. Scanning was performed with 2θ ranging from 5° to 50°. The IR spectra were recorded with a NICOLET 70S spectrometer (KBr pellet technique) from 400 to 4000 cm⁻¹.

3. Synthesis of Complexes 1-6.

3.1 Synthesis of [R₂-(S, S)-BOZ]Pd(II)Me (R = CH(CH₃)₂) (**1**).

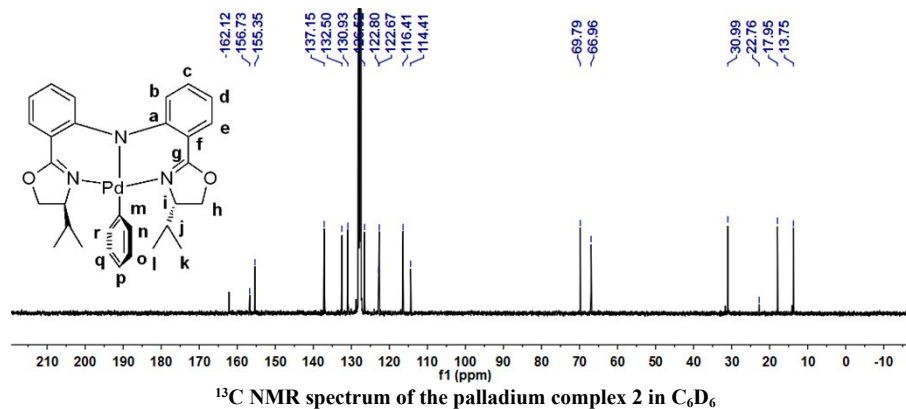
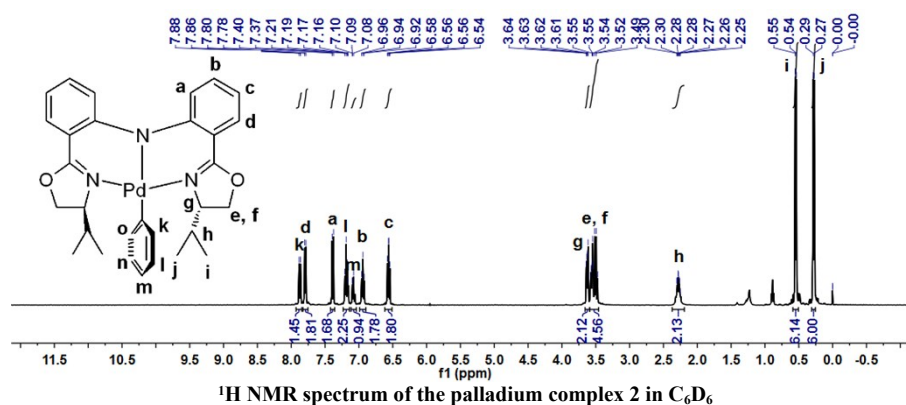
A solution of [((CH(CH₃)₂)₂-(S, S)-BOZ)PdCl] (213 mg, 0.4 mmol) in THF (10 mL) was cooled to -30 °C, and a solution of MeLi in THF (1M/L, 0.4 mL) was added dropwise in the glovebox. The resulting solution was stirred for 3 h at room temperature and then filtered. The filtrate was evaporated and the red solid residue was washed with pentane several times (3×3 mL). After dried by vacuum, the residue was recrystallized from THF and hexane at -33 °C to give **1** as orange-red solid (134 mg, 66%). ¹H NMR (400 MHz, C₆D₆) δ 7.80 (dd, 2H, ArH), 7.33 (d, 2H, ArH), 6.92-6.96 (m, 2H, ArH), 6.54 (t, 2H, ArH), 4.14-4.19 (m, 2H, CH₂ in oxazoline), 3.68-3.71 (m, 2H, CH₂ in oxazoline), 3.52 (t, 2H, CH in oxazoline), 2.31-2.35 (m, 2H, CHMe₂), 0.64 (s, 3H, PdMe), 0.62 (d, 6H, CHMe₂), 0.54 (d, 6H, CHMe₂). ¹³C NMR (100 MHz, C₆D₆) δ 161.90, 155.34

(C in oxazoline), 132.46, 130.90, 122.17, 116.00, 114.78 (ArC), 67.99 (CH₂ in oxazoline), 66.83 (CH in oxazoline), 31.37 (CHMe₂), 18.02 (CHMe₂), 14.05 (CHMe₂), -8.07 (PdMe).



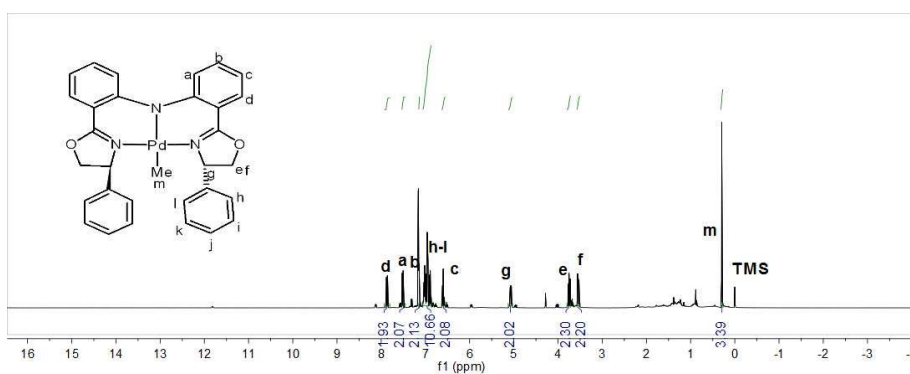
3.2 Synthesis of [R₂-(S, S)-BOZ]Pd(II)Ph (R = CH(CH₃)₂) (2).

To a solution of [(CH(CH₃)₂)₂-(S, S)-BOZ]PdCl (106.5 mg, 0.2 mmol) in THF (10 mL) cooled to -78 °C was added 0.21 mL of a 1M/L solution of PhLi in THF (0.21 mmol) dropwise under the nitrogen atmosphere. Over 0.5 h the temperature was allowed to rise to 25 °C. The resulting solution was stirred for 12 h at room temperature and then filtered in the glovebox. The filtrate was evaporated and the yellow solid residue was washed with pentane several times (3×3 mL). After dried by vacuum, the residue was recrystallized from THF and hexane at -33 °C to give **2** as yellow solid (80 mg, 70%). ¹H NMR (400 MHz, C₆D₆) δ 7.87 (dd, 2H, ArH), 7.79 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.19 (t, 2H, ArH), 7.08-7.16 (m, 1H, ArH), 6.94 (t, 2H, ArH), 6.53-6.59 (m, 2H, ArH), 3.61-3.64 (m, 2H, CH in oxazoline), 3.47-3.58 (m, 4H, CH₂ in oxazoline), 2.25-2.30 (m, 2H, CHMe₂), 0.54 (d, 6H, CHMe₂), 0.28 (d, 6H, CHMe₂). ¹³C NMR (100 MHz, C₆D₆) δ 162.12, 156.73 (C in oxazoline), 155.35, 137.15, 132.50, 130.93, 126.52, 122.80, 116.41, 114.41 (ArC), 69.79 (CH₂ in oxazoline), 66.96 (CH in oxazoline), 22.76 (CHMe₂), 17.95 (CHMe₂), 13.75 (CHMe₂).

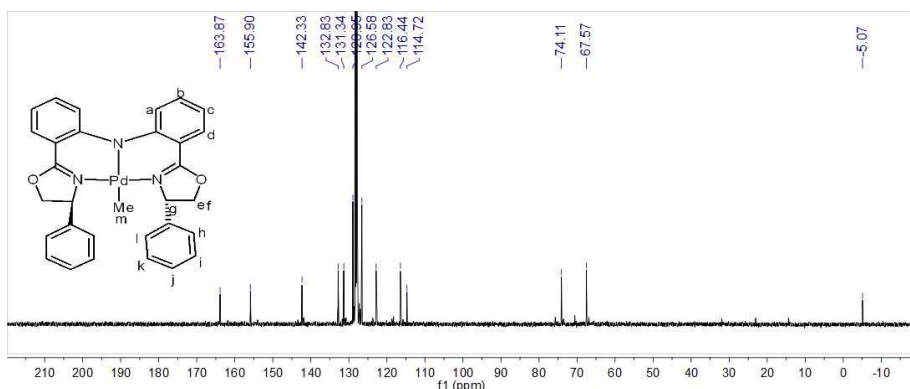


3.3 Synthesis of [R₂-(S, S)-BOZ]Pd(II)Me (R = Ph) (3).

A solution of [Ph₂-(S, S)-BOZ]PdCl (240 mg, 0.4 mmol) in THF (10 mL) was cooled to -30 °C, and a solution of MeLi in THF (1M/L, 0.4 mL) was added dropwise in the glovebox. The resulting solution was stirred for 6 h at room temperature and then filtered. The filtrate was evaporated and the red solid residue was washed with pentane several times (3×3 mL). After dried by vacuum, the residue was recrystallized from THF and hexane at -33 °C to give **3** as orange-red solid (134 mg, 73%). ¹H NMR (400 MHz, C₆D₆) δ 7.86 (dd, 2H, ArH), 7.51 (d, 2H, ArH), 7.12-7.14 (m, 2H, ArH), 6.86-7.04 (m, 10H, ArH), 6.55-6.63 (m, 2H, ArH), 5.07 (q, 2H, CH₂ in oxazoline), 3.71-3.77 (m, 2H, CH in oxazoline), 3.54 (q, 2H, CH₂ in oxazoline), 0.29 (s, 3H, PdMe). ¹³C NMR (100 MHz, C₆D₆) δ 163.87, 155.90 (C in oxazoline), 142.33, 132.83, 131.34, 128.95, 126.58, 122.83, 116.44, 114.72 (ArC), 74.11 (CH₂ in oxazoline), 67.57 (CH in oxazoline), -5.07 (PdMe).



¹H NMR spectrum of the palladium complex 3 in C₆D₆



¹³C NMR spectrum of the palladium complex 3 in C₆D₆

3.4 Synthesis of [R₂-(S, S)-BOZ]Ni(II)Me (R = Ph) (4).

A solution of [Ph₂-(S, S)-BOZ]NiCl (276 mg, 0.5 mmol) in THF (10 mL) was cooled to -30 °C, and a solution of MeLi in THF (1M/L, 0.4 mL) was added dropwise in the glovebox. The resulting solution was stirred for 16 h at room temperature. 1,4-Dioxane (86 μL, 1 mmol) was added, the mixture was stirred for another hour, and then filtered. The filtrate was evaporated and the red solid residue was washed with pentane several times (3×3 mL). After dried by vacuum, the residue was recrystallized from THF and hexane at -33 °C to give **4** as orange-red solid. ¹H NMR (400 MHz, C₆D₆) δ 7.77 (dd, 2H, ArH), 7.23-7.34 (m, 6H, ArH), 6.99-7.11 (m, 6H, ArH), 6.90-6.97 (m, 2H, ArH), 6.58-6.68 (m, 2H, ArH), 4.74 (q, 2H, CH₂ in oxazoline), 3.64 (t, 2H, CH in oxazoline), 3.46 (q, 2H, CH₂ in oxazoline), -0.67 (s, 3H, NiMe). ¹³C NMR (100 MHz, C₆D₆) δ 162.55, 155.53 (C in oxazoline), 142.79, 132.50, 129.78, 129.05, 126.54, 122.88, 116.52, 115.35 (ArC), 73.93 (CH₂ in oxazoline), 66.69 (CH in oxazoline), -13.14 (NiMe).

3.5 Synthesis of [R₂-(S, S)-BOZ]Ni(II)Me (R = CH(CH₃)₂) (5).

The chiral R₂-(S, S)-bis(oxazoline) nickel(II) alkyl complex [R₂-(S,S)-BOZ]Ni-Me (R = CH(CH₃)₂) (**5**) was synthesized according to the literature.² ¹H NMR (400 MHz, C₆D₆) δ 7.79 (dd, 2H, ArH), 7.18 (d, 2H, ArH), 6.91-6.98 (m, 2H, ArH), 6.52-6.60 (m, 2H, ArH), 3.71-3.81 (m, 2H, CH₂ in oxazoline), 3.55-3.62 (m, 2H, CH₂ in oxazoline), 3.48 (t, 2H, CH in oxazoline), 2.28-2.38 (m, 2H, CHMe₂), 0.75 (d, 6H, CHMe₂), 0.60 (d, 6H, CHMe₂), -0.48 (s, 3H, NiMe).

3.6 Synthesis of $[R_2-(S, S)\text{-BOZ}]\text{Ni(II)Ph}$ ($R = \text{CH}(\text{CH}_3)_2$) (**6**).

The chiral R_2 -(S, S)-bis(oxazoline) nickel(II) alkyl complex $[R_2-(S,S)\text{-BOZ}]\text{Ni-Ph}$ ($R = \text{CH}(\text{CH}_3)_2$) (**6**) was synthesized according to the literature.² $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 7.81-7.91 (m, 4H, ArH), 7.46 (dd, 1H, ArH), 7.20-7.26 (m, 2H, ArH), 7.07 (t, 2H, ArH), 6.89-7.0 (m, 2H, ArH), 6.56-6.62 (m, 2H, ArH), 3.41-3.55 (m, 4H, CH_2 in oxazoline), 2.75-2.83 (m, 2H, CH in oxazoline), 2.26-2.41 (m, 2H, CHMe_2), 0.58 (d, 6H, CHMe_2), 0.35 (d, 6H, CHMe_2).

$^1\text{H NMR}$ spectra of the methyl complexes **1**, **3–5** displayed that the new singlets at high field assigned for the methyl protons of the Pd–Me or Ni–Me group appeared at δ 0.64, 0.29, -0.67, -0.48 ppm (s, 3H), respectively. Moreover, the new chemical shifts found in the aromatic region (δ 6.5–8.0 ppm, m, 5H) can be easily identified the existence of Pd–Ph or Ni–Ph bond in the phenyl complexes **2** and **6**. In addition, the methylene and methine groups belonging the oxazoline ring also appeared at the different positions in comparison with those of the corresponding Pd(II) and Ni(II) chloride complexes, indeed implying the formation of the Pd(II) and Ni(II) alkyl complexes **1–6**. Two different multiplets for the methylene protons of the oxazolonyl ring between 2.1 and 5.5 ppm integrating for 4 protons were observed, suggesting a symmetry in the chelating (S, S)-bis(oxazoline) amine ligand of these alkyl complexes **1–6**.

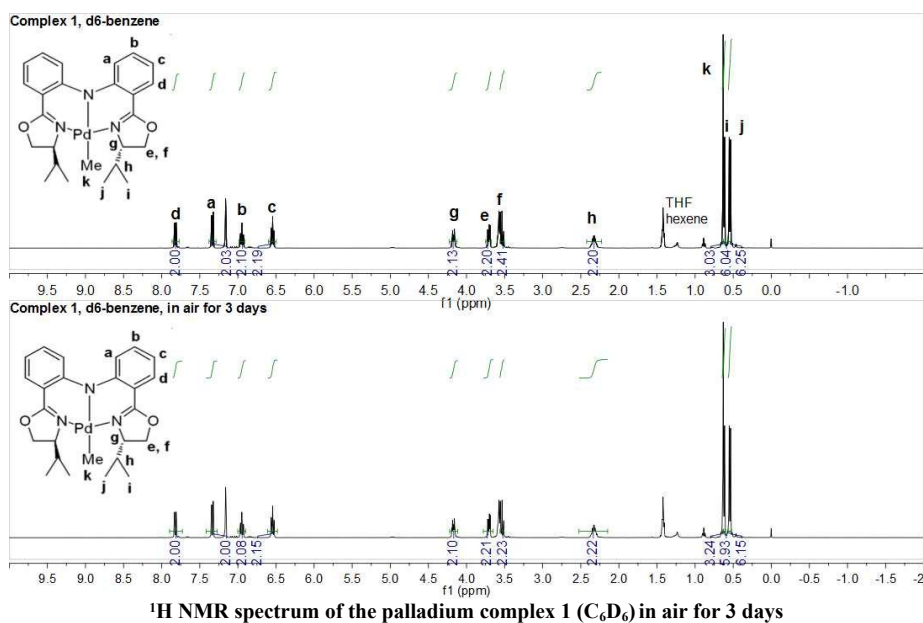
4. Table S1 Vinyl polymerization of norbornene by chiral Ni alkyl complexes/cocatalyst systems in nitrogen^a

entry	Cat. (μmol)	cocat. ^[b]	Sol. ^[c]	[Al]/[M]	[A]/[M]	[NB]/[M]	<i>t</i> (min)	T ($^\circ\text{C}$)	Y (%)	A ^[d]
1	4 (1.0)	A /AlMe ₃	T	15	10	10000	60	25	5	0.05
2	4 (1.0)	B /Al ⁱ Bu ₃	T	15	10	10000	60	25	-	-
3	4 (1.0)	C /AlMe ₃	T	15	10	10000	60	25	-	-
4	5 (1.0)	A /AlMe ₃	T	15	10	10000	60	25	5	0.05
5	5 (1.0)	B /Al ⁱ Bu ₃	T	15	10	10000	60	25	-	-
6	5 (1.0)	C /AlMe ₃	T	15	10	10000	60	25	-	-
7	6 (1.0)	A /AlMe ₃	T	15	10	10000	60	25	40	0.4
8	6 (1.0)	B /Al ⁱ Bu ₃	T	15	10	10000	60	25	11	0.1
9	6 (1.0)	C /AlMe ₃	T	15	10	10000	60	25	-	-

[a] Conditions: total volume 5 mL. [b] Activator: $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (A), $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (B), borane $\text{B}(\text{C}_6\text{F}_5)_3$ (C). [c]

T = toluene. [d] Activity: 10^6 g PNB/mol_M•h.

5. Characterization of the palladium complex **1** (C_6D_6) in air for 3 days



The ¹H NMR spectra displays that the chemical shifts of all peaks of Pd complex **1** didn't change after stored in air and water for several days in the solid state, indicating that the Pd complex is very stable in the presence of oxygen and moisture.

6. A Typical Procedure for Norbornene (NB) Polymerization by Complex 1/Activator Binary System in Air (Table 2, entry 4).

Under air atmosphere, the catalyst precursor (1.0×10^{-6} mol, 0.1 mL of 10 mmol/L in 1,2-dichlorobenzene) was added into a 25 mL round-bottom flask with a magnetic stirrer. Then norbornene (0.010 mol, 0.94 g) and 1,2-dichlorobenzene (4.9 mL) was charged into this flask. After 3 min, the activator ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ 9.23 mg (10 μmol)) was added. The mixture was magnetically stirred for 4 min. Then the reaction was terminated by adding 15 mL of acidified ethanol (10/1 ethanol/HCl, v/v). The precipitate of polynorbornene was filtered off, washed with ethanol (3×10 mL), and dried to constant weight at 60 °C under vacuum as a white powder.

7. A Typical Procedure for Norbornene (NB) Polymerization by Complex 1/Activator Binary System in Air and Water (Table 2, entry 22).

Under air atmosphere, the catalyst precursor (1.0×10^{-6} mol, 0.1 mL of 10 mmol/L in 1,2-dichlorobenzene) was added into a 25 mL round-bottom flask with a magnetic stirrer. Then unpretreated norbornene (0.010 mol, 0.94 g) and unpretreated technical grade 1,2-dichlorobenzene (4.4 mL) were charged into this flask. Distilled and non-degassed water (0.5 mL) were added (total volume 5 mL). After 3 min, the activator ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ 9.23 mg (10 μmol)) was added. The mixture was magnetically stirred for 4 min at the given temperature. Then the reaction was terminated by adding 15 mL of acidified ethanol (10/1 ethanol/HCl, v/v). The precipitate of polynorbornene was filtered off, washed with ethanol (3×10 mL), and dried to constant

weight at 60 °C under vacuum as a white powder.

8. X-ray Crystallographic Analysis.

A crystal was sealed in oil under a microscope in the glove box. Data collections were performed at 173K on a Bruker-AXS X-ray diffractometer with a CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL-97 program. Refinements were performed on F2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. **CCDC-988840 (1)** and contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystallographic data and refinement for complexes **1**.

	1
Empirical formula	C ₂₉ H ₃₁ N ₃ O ₃ Pd
Formula weight	575.97
Wavelength	0.71073 Å
Crystal system	Tetragonal
space group	<i>P4(1)2(1)2</i>
<i>a</i> (Å)	9.1556(3)
<i>b</i> (Å)	9.1556(3)
<i>c</i> (Å)	66.051(4)
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å ³)	5536.7(4)
<i>Z</i>	8
D _{calcd} (Mg/m ³)	1.382
μ (mm ⁻¹)	0.704
F(000)	2368
Crystal size (mm)	0.45 x 0.43 x 0.42
θ range, (°)	2.25-25.02
limiting indices	-10 \leq h \leq 10, -10 \leq k \leq 10, -78 \leq l \leq 56

no. of reflns collected	27346
no. of indep reflns	4875 [$R_{\text{int}} = 0.0590$]
completeness to theta	99.8 %
max. and min. transmission	0.7565 / 0.7425
no. of data / restraints / parameters	4875 / 0 / 330
Goodness-of-fit on F^2	1.176
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0492, wR_2 = 0.1172$
R indices (all data)	$R_1 = 0.0534, wR_2 = 0.1193$
Absolute structure parameter	0.05(5)
Largest diff. peak and hole, $e \text{ \AA}^{-3}$	1.490 / -0.806

9. The IR spectra display that there are no signals at 1620–1680, 966 and 735 cm^{-1} which are regarded as traces of double bond, suggesting the formation of vinylic-type polynorbornenes.

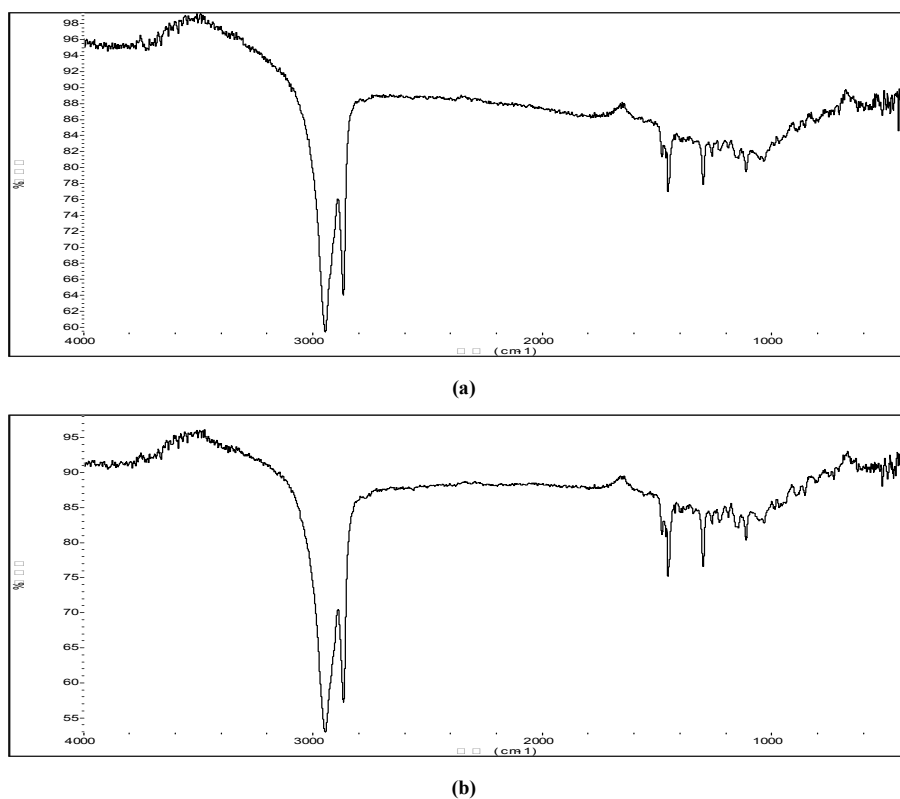


Figure 1. IR spectra of PNBs obtained by chiral palladium complexes 1–2/cocatalysts systems under air atmosphere in Table 1 (a: entry 1, b: entry 5).

10.

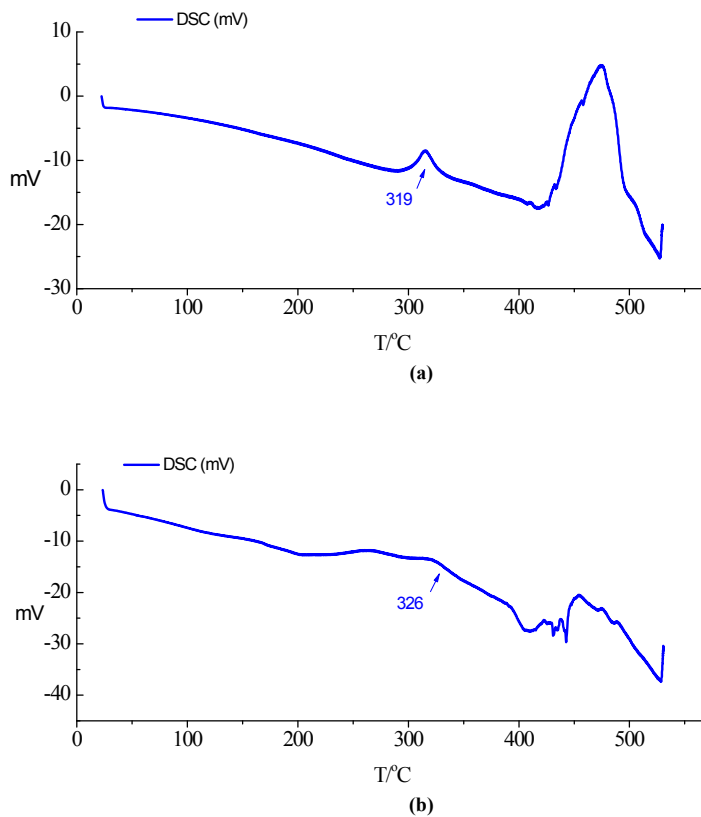


Figure 2. DSC curves of PNBs obtained by the complex **1**/activators in Table 1 (**a**: entry 3, **b**: entry 24).

DSC curves revealed the glass transition temperatures (T_g) of these PNBs in the range of 316–318 °C, which indicated that the PNBs obtained by these catalytic systems had good thermal stability.

11.

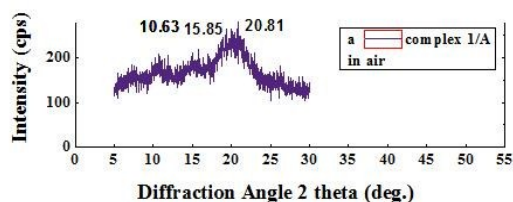


Figure 3. WAXD diagram of PNBs obtained by chiral palladium methyl complex **1** in Table 1 (**a**: entry 2).

Figure 3 displayed the WAXD diagram of the polynorbornenes obtained by chiral palladium methyl complex **1** in the presence of borate **A** in air. The WAXD spectra revealed no obvious traces of Bragg reflections, and, therefore, the polymers are amorphous, but have a short-range order and high packing density.

12.

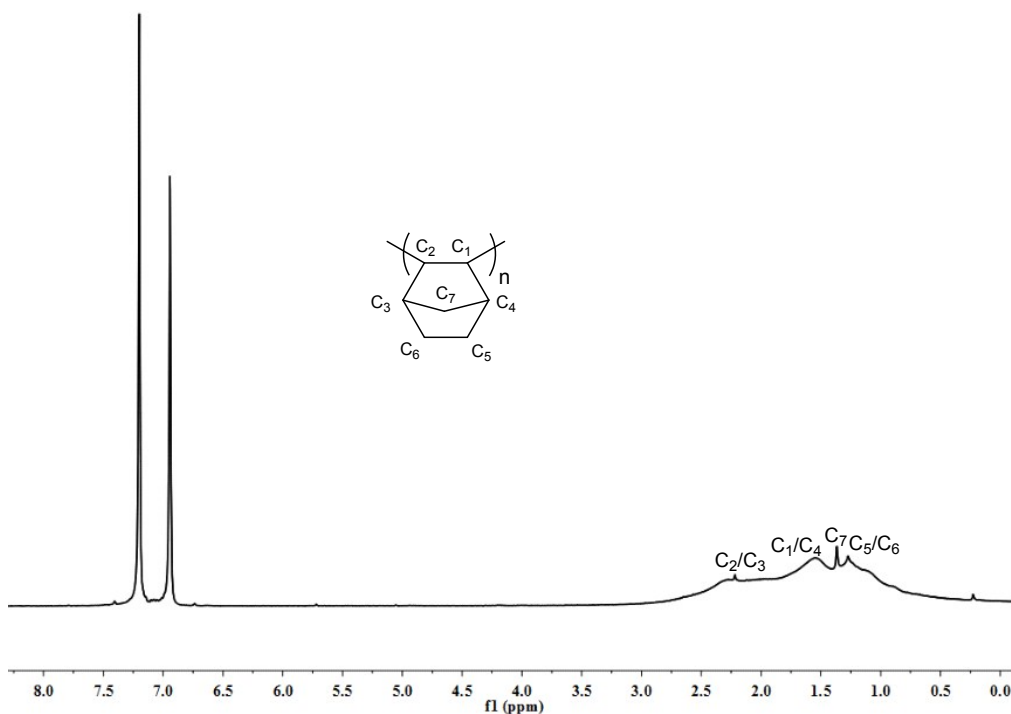


Figure 4. ^1H NMR spectra of PNB.

13. **Figure 4.** ^1H NMR spectra of PNB.

The oligonorbornene had been prepared under low [norbornene]/[catalyst] molar ratio (ca. [norbornene]/[catalyst] = 15). However, the oligonorbornene obtained had also bad solubility in toluene at 25 °C. The ^1H NMR spectrum of the oligonorbornene in $o\text{-C}_6\text{D}_4\text{Cl}_2$ indicate completely vinylic microstructures. In the ^1H NMR spectrum, there appear four group resonance peaks of typical vinyl-type addition PNBs in the region from 0.5 to 3.2 ppm. The resonance peaks at 0.8-1.8 ppm correspond to nonbridging CH_2 groups (C_5/C_6), and the peak at 1.30 ppm corresponds to bridgehead CH groups (C_7). The resonance peak at 1.63-1.89 ppm corresponds to bridgehead CH groups (C_1/C_4). The resonance peak at 2.1-2.4 ppm corresponds to the backbone connecting CH groups (C_2/C_3). In addition, the absence of a resonance at 5.0-6.0 ppm indicates no double bonds, and these are typical resonance peaks for metathesis-type PNBs.³

Reference

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- (2) I. Kieltsch, G. G. Dubinina, C. Hamacher, A. Kaiser, J. T. Nieto, J. M. Hutchison, A. Klein, Y. Budnikova and D. A. Vacic, *Organometallics*, 2010, **29**, 1451.
- (3) X. He and Q. Wu, *J. Appl. Polym. Sci.*, 2006, **101**, 4172.