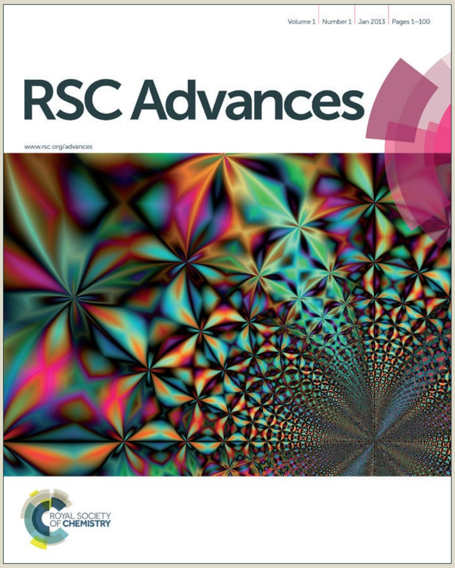
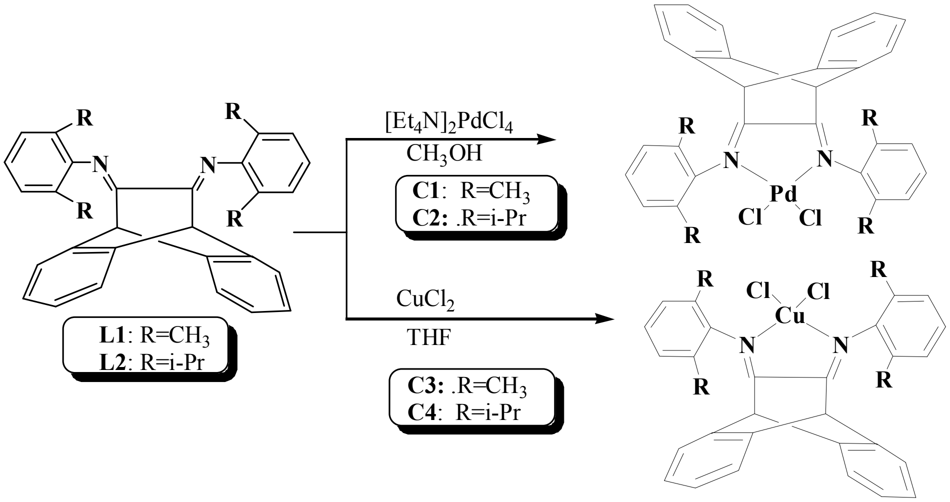
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

The polymerization of norbornene (NB) to produce vinyl-type polynorbornene can be accomplished by metal complexes based on nickel,[1-3] palladium,[4-6] chromium,[7] zirconium,[8-9] and cobalt.[10] Vinyl-type PNB is of interest due to its good mechanical strength, heat resistivity, and optical transparency for deep ultraviolet (193 nm) photoresist binder resins in lithographic processes,[11] interlevel dielectrics in microelectronics applications, or as a cover layer for liquid-crystal displays.[12-15] However, the obvious disadvantages of the homopolymer polynorbornene (PNB) are poor solubility in common organic solvents and the poor adhesion. Important extensions have been accomplished by vinyl-addition copolymerization of norbornene/functionalized norbornenes to improve the solubility. [16-18] In order to fully exploit the potential of this interesting class of polymers, catalyst activities, control of molecular weight, and functionalization have to be improved. Therefore, catalyst design is still a challenge. Since bulky α-diimine nickel and palladium complexes have been successfully developed by Brookhart and his collaborators, the utilization of α-diimine complexes of Ni(II) or Pd(II) for norbornene vinyl-addition polymerization in the present of MAO, modified MAO (MMAO), has attached much interest in both academic and industrial fields over the past dozen years. [19-20] There were a number of nickel and palladium complexes bearing a bidentate nitrogen ligand have been reported as a catalyst for the olefin polymerization such as diimine,[21-22] pyridylimine[23] and bipyridine.[24-26] Much of those work focused on changing the N-bound aryl group[27-28] or modifying the backbone,[29-33] including the use of axial donating diimine ligands.[34-36] In general, these complexes are activated by methylaluminoxane (MAO) or are cationic complexes with weakly coordinating counterions. So, we are interested in synthesizing novel late-transitionmetal catalysts and homopolymerizing NB to study the relationship between the catalyst structure and activity. In this paper, as shown in Scheme **1**, we designed and synthesized a series of palladium(II) and copper(II) chloride complexes (**C1-C4**) bearing α-diimine ligands, 9,10-dihydro-9,10-ethanoanthracene-11,12-diimine, which have bulky substituted backbone, good steric effect, strong rigid and good symmetry. Those complexes were used for norbornene vinyl-addition polymerization after activation with MAO. In addition, **C2** was selected as catalyst precursor for vinyl-addition copolymerization of norbornene (NB) with 2-butyloxymethylene norbornene (BN).



Scheme 1. Syntheses of palladium(II) and copper(II) chloride complexes bearing bulky α-diimine ligands

2. Experimental section

2.1 Materials

All the reactions were performed under an atmosphere of dry and oxygen-free argon using standard vacuum or Schlenk techniques, or under a nitrogen atmosphere in a glove box (MBraun). Chlorobenzene (Aldrich) was dried over P_2O_5 and distilled under nitrogen. Tetrahydrofuran (Acros), pentane (Aladdin) and hexane (Aldrich) were refluxed over metallic sodium for 24 hours before being used. Norbornrene (NB) was purchased from Alfa Aesar and was dried over CaH_2 and purified by trap-to-trap distillation before using, then prepared as a solution (4.25 mol/L) in chlorobenzene. 2-butyloxymethylene norbornene (BN) was synthesized by referring to our group previously reported method.[37] $PdCl_2$ (Aldrich), $CuCl_2$ (Acros) and MAO (10% solution in toluene, 1.5mol/L, Aladdin) were used as received. Other commercially available reagents were purchased and used without further purification.

2.2 Measurements

The intensity data of the single crystals were collected on the CCD-Bruker Smart APEX II system. Elemental analyses (EA) were characterized by means of elemental analysis with Vario Elementary III. The nuclear magnetic resonance (^1H NMR and ^{13}C NMR) of the palladium(II) and copper(II) complexes and copolymers were obtained on Bruker ARX 400 NMR(400 MHz) spectrometer at ambient temperature with

$CDCl_3$ as the solvent and tetramethylsilane (TMS, δ=0) as an internal reference. The XT4A melting point measure instrument (BeiJing KeYi electro-optic instrument factory, China) was used to test the melting point temperature. The FTIR spectra were recorded by a Shimadzu IR Prestige-21 FTIR spectrophotometer. The wide-angle X-ray diffraction (WXRD) curves were provided on a Bruker D8 Focus X-ray diffractometer, operating at 40 kV and 40 mA with a copper target (λ=1.54 Å) and at a scanning rate of 2°/min from 2° to 60°. The molecular weight and molecular weight distribution (MWD) of the polymers were carried out by gel permeation chromatography (PL-GPC220) with a refractive index detector. 1,2,4-trichlorobenzene as an eluent with a flow rate of 1.0 $mLmin^{-1}$ and the detector at 150 °C. Thermo gravimetric analysis (TGA) was performed on a TAQ600 SDT for thermogravimetry at a heating rate of 10 °C min^{-1} under nitrogen.

2.3 Syntheses of bulky α-diimine palladium(II) and copper(II) chloride complexes (C1-C4)

Bulky α-diimine ligands, 9,10-dihydro-9,10-ethanoanthracene-11,12-diimine (**L1-L2**), were synthesized referring to our group previously reported methods.[38] The α-diimine palladium(II) chloride complexes (**C1-C2**) were synthesized by the reaction of $[(C_2H_5)_4N]_2PdCl_4$ with the corresponding ligand in methanol. A typical synthetic procedure for **C1** could be described as follows: 0.15 mmol $[(C_2H_5)_4N]_2PdCl_4$, 0.15 mmol of ligand **L1** and methanol (30 mL) were in a Schlenk flask and stirred at room temperature for 12 h and 40 mL of absolute pentane was added. The yellow crystal complex was crystallized from the mixture of methanol and pentane in 70% yield. M_p: 326-327 °C. Elemental analysis (%), found: C, 62.18; H, 4.59 ; N, 4.50; calcd: C, 62.20; H, 4.57; N, 4.53. ^1H NMR($CDCl_3$, δ, ppm): 1.29(s, 12H, CH_3), 5.12(s, 2H, CH), 6.21-7.47(m, 14H)。 ^{13}C NMR($CDCl_3$, δ, ppm): 18.23, 38.65, 124.45, 125.81, 127.46, 128.64, 129.33, 130.02, 138.71, 139.23,142.26, 176.33.

C2 was obtained as a dark yellow crystal in 73% yield. Single crystals of **C2** was grown by diffusing a diethylether layer onto its methanol solutions. M_p： 335-336 ºC. Elemental analysis (%), found: C, 65.81; H,6.11 ; N, 3.80; calcd: C, 65.80; H, 6.07; N, 3.84. ^{1}H NMR(CDCl$_3$, δ, ppm): 1.13(d, 24H, CH$_3$), 3.28(m, 4H, CH)，4.83(s, 2H, CH), 7.09-7.45(m, 14H).^{13}C NMR(CDCl$_3$, δ, ppm):18.38, 127.55, 128.62, 131.68, 136.76, 143.68, 175.84.

C3 was readily prepared by mixing ligand **L1** (0.10 mmol) and anhydrous CuCl$_2$ (0.1 mmol) in 15 mL THF and stirring at room temperature for 48 hours. The formed yellow-brown precipitate was filtered, washed with 3 × 5 mL THF and dried in Vacuo. Yield 81%. Crystals of **C3** suitable for an X-ray structure determination were grown from a dichloromethane solution of the complex layered with pentane. M$_p$: 322-323ºC. Elemental analysis (%), found: C,66.82; H,4.89 ; N, 4.85; calcd: C, 66.84; H, 4.91; N, 4.87. H NMR(CDCl$_3$, δ, ppm): 1.82(s, 12H, CH$_3$), 4.84(s, 2H,CH), 6.70-7.24(m, 14H). ^{13}C NMR(CDCl$_3$, δ, ppm):17.89, 30.32, 121.43,123.56,126.22, 127.86, 127.82, 128.03, 134.28, 143.64, 167.21.

C4 was obtained as a black crystal in 75% yield. Crystals of **C4** suitable for an X-ray structure determination were grown from a dichloromethane solution of the complex layered with hexane. M$_p$: 340-341ºC. ^{1}H NMR(CDCl$_3$, δ, ppm): 1.26 (d, 24H, CH$_3$), 3.72(m, 4H, CH)，4.76(s, 2H, CH), 6.96-7.52(m, 14H). ^{13}C NMR(CDCl$_3$, δ, ppm): 25.11, 30.45, 121.19,124.35, 125.76, 126.38, 127.55, 128.46, 130.72, 135.54, 147.28, 167.89. Elemental analysis (%), found: C, 69.90; H, 6.46 ; N, 4.06; calcd: C, 69.91; H,6.45; N, 4.08.

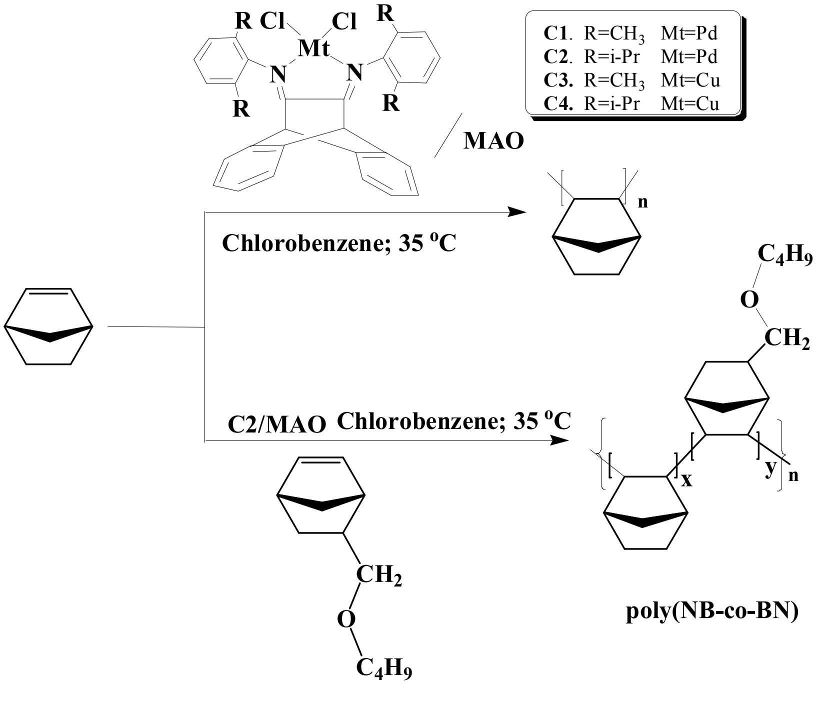
The ^{1}H NMR and ^{13}C NMR spectra of **C1**,**C2**,**C3** and **C4** are shown in **Fig.S1-Fig.S8** in Electronic Supplementary Material (ESI).

2.4 Crystal structure determination

The X-ray diffraction data of the single crystals were obtained with the ω-2θ scan mode on a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073). The structures were solved using direct methods, and further refinements with full-matrix least-squares on F^2 were obtained with the SHELXTL program package. All non-hydrogen atoms were refined an isotropically and hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

2.5 Homopolymerization of Norbornene

Bulky α-diimine palladium(II) and copper(II) chloride complexes (**C1**-**C4**) were selected as catalyst precursor for the homopolymerization of norbornene (NB). All of procedures were carried out under a purified nitrogen atmosphere. A typical procedure is as follows: 6.6 mL (1.5 mol/L) toluene solution of MAO, 2.35mL (0.0425mol/L) chlorobenzene solution of NB and 4.05 mL chlorobenzene were placed in a Schlenk flask (100 mL) with a strong stirrer under a nitrogen atmosphere. After stirring at 35 °C for 1min, 5 μmol (3.65×10^{-3} g) of the **C2** complex in 2 mL chlorobenzene was added to the mixture via a syringe and the reaction was initiated. The total volume was kept constant at 15 mL. After 30 minutes, acidic ethanol (ethanol–HCl = 9/1) was added to terminate the reaction. The PNB was isolated by filtration,washed with ethanol, dried at 50 °C for 24 h under vacuum. The condition of other NB homopolymerization setup is similar to this procedure except that the amount of different co-cat was added at the beginning of the process.The homopolymerization procedure was shown in Scheme **2**.



Scheme **2.** Norbornene polymerization and copolymerization catalyzed by bulky α-diimine palladium(II) and copper(II) chloride complexes

2.6 Copolymerization of Norbornene and 2-butyloxymethylene norbornene

C2 was selected as catalyst precursor for the copolymerization of norbornene (NB) with 2-butyloxymethylene norbornene (BN). A typical copolymerization procedure was as follows: 6.6 mL (1.5 mol/L) toluene solution of MAO, 0.94 mL (0.0425 mol/L) chlorobenzene solution of NB, 0.4 mL 2-butyloxymethylene norbornene (BN) and 5.06 mL chlorobenzene were placed in a Schlenk flask (100 mL) with a strong stirrer under a nitrogen atmosphere. After stirring at 35 °C for 1min, 5 μmol (3.65×10^{-3} g) of the **C2** complex in 2 mL chlorobenzene was added to the mixture via a syringe and the reaction was initiated. The total volume was kept constant at 15 mL. After 30 minutes, acidic ethanol (ethanol–HCl = 9/1) was added to terminate the reaction. The polymer was isolated by filtration, washed with ethanol, dried at 50 °C for 24 h under vacuum. The condition of other copolymerization reaction of NB with BN is similar to this procedure except that the amount of NB and BN was added at the beginning of the process. The copolymerization procedure was shown in Scheme **2**.

3. Results and discussion

3.1 Ligands and complexes syntheses

Bulky **α**-diimine palladium(II) chloride complexes (**C1-C2**) and copper(II) chloride complexes (**C3-C4**) were characterized by elemental analysis, X-ray crystallography and NMR spectroscopy. Although mononuclear Cu(II) compounds are paramagnetic usually, the copper complexes we synthesized can be characterized by NMR spectroscopy (**Fig. S1-S8** in ESI). It is interesting that obvious shifted aromatic signals cannot be found from the ^{1}H NMR spectroscopy, which is different from that Gibson reported.[39] To the best of our knowledge, we speculate the potential cause that copper chloride complexes (**C3-C4**) bearing bulky ligands have good steric effect for the existence of symmetrical benzene ring and strong rigidity. At the same time, conjugative effect and π–π stacking effect between backbone benzene ring and substituted benzene ring may reduce the aromatic signals shifted. From the ^{1}H NMR spectroscopy of **C3** and **C4**, the data of typical paramagnetic species with broad of

Cu(II) complexes are not found.[39] Under N_2 atmosphere, complexes **C1**-C4 were stable at room temperature for weeks. The crystal structures of complexes **C1**. 2CH$_3$OH, **C2**, **C3** and **C4** were solved by X-ray diffraction studies (Fig. **1-4**).The crystallographic data were summarized in Table **1**. CIF data complexes can be available as Supporting Information. Table **2** listed the selected bond lengths and angles of complexes.

In all these complexes, the palladium and copper atom are in a slightly distorted square planar environment within the standard range for this type of complex. The Mt (Mt=Pd, Cu) center is coordinated by two chloride atoms and by two nitrogen atoms of 9,10-dihydro-9,10-ethanoanthracene-11,12-diimine ligand. This coordination mode is similar to the corresponding nickel complexes our group previously reported.[38] Bond lengths of Mt-N (Mt=Pd, Cu) are very close, from 2.020 to 2.071 Å, Mt-Cl (Mt=Pd, Cu), from 2.1815 to 2.2672 Å. The N–Mt–N (Mt=Pd, Cu) angles are between 79.7(2)° and 81.01(10)°. The Cl–Mt–Cl (Mt=Pd, Cu) angles are between 90.60(4)° and 104.37(5)°.

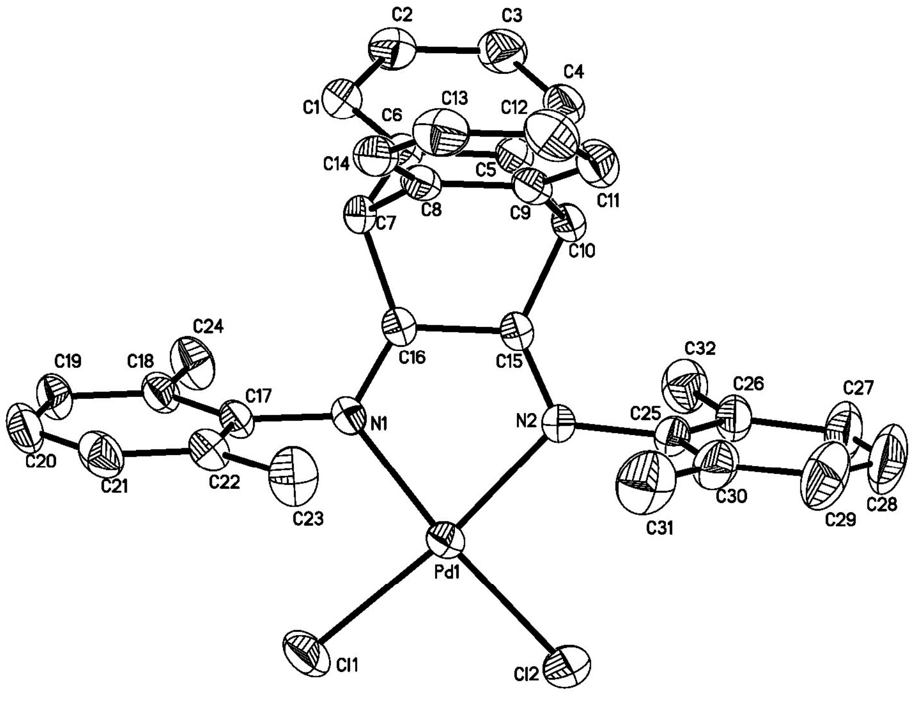


Fig. **1.** ORTEP plots of **C1** showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level, Hydrogen atoms and the solvent are omitted for clarity.

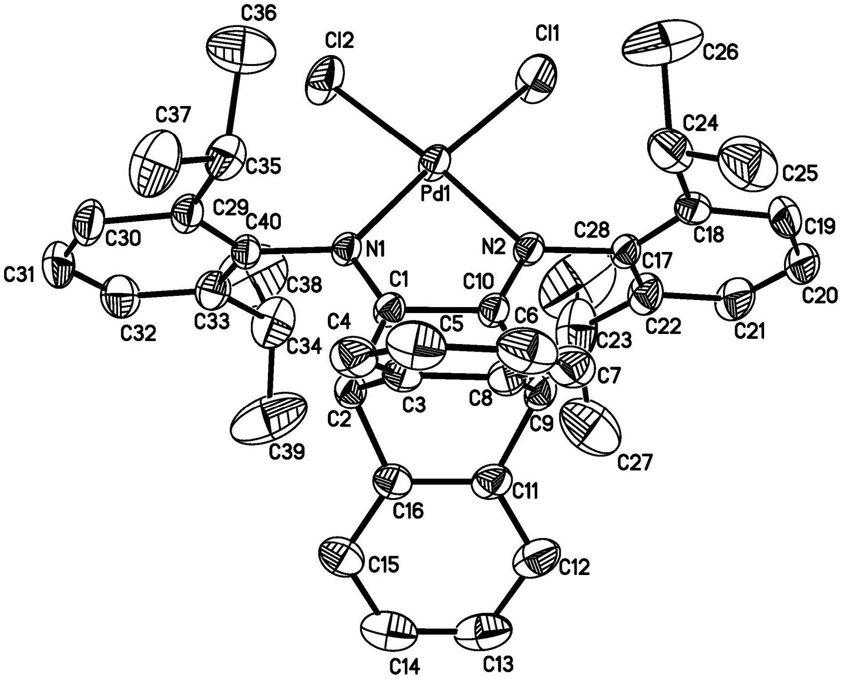


Fig. **2.** ORTEP plots of **C2** showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level, Hydrogen atoms and the solvent are omitted for clarity.

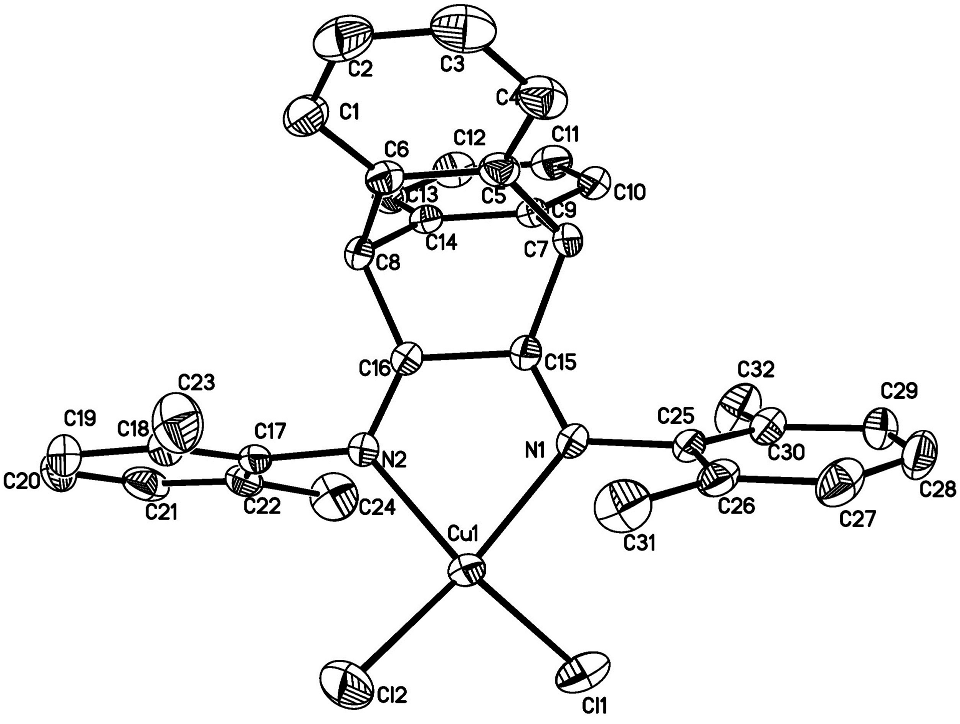


Fig. **3.** ORTEP plots of **C3** showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level, Hydrogen atoms and the solvent are omitted for clarity.

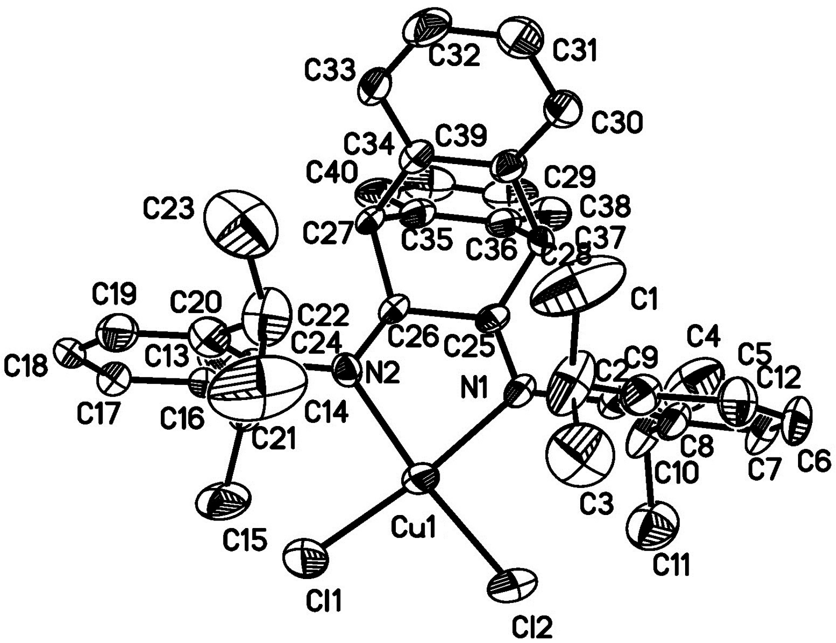


Fig. **4.** ORTEP plots of **C4** showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level, Hydrogen atoms and the solvent are omitted for clarity.

Table **1.** Crystallographic data for the complexes

	C1	**C2**	**C3**	**C4**
Empirical formula	$C_{32}H_{28}Cl_2N_2Pd.CH_3OH.H_2O$	$C_{40}H_{44}Cl_2N_2Pd$	$C_{32}H_{28}Cl_2N_2Cu$	$2[C_{40}H_{44}Cl_2N_2Cu.CH_2Cl_2]$
Formula weight	667.92	730.07	575.00	1544.28
Crystal color	Yellow	Yellow	Black	Black
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic P2(1)/c	Monoclinic, Cc	Orthorhombic, Pbca	Monoclinic, P2(1)
a (Å)	14.638(2)	22.5512(15)	17.819(2)	12.373(2)
b (Å)	10.8203(17)	10.8570(7)	16.0039(18)	16.272(3)
c (Å)	21.054(3)	17.8588(12)	19.235(2)	19.788(4)
α (deg)	90	90	90	90
β (deg)	103.524(2)	122.1150(10)	90	99.265(3)
γ (deg)	90	90	90	90
Volume ($Å^3$)	3242.2(9)	3703.4(4)	5485.4(11)	3932.0(13)
Z, Calculated density(Mg m^{-3})	4, 1.397	4, 1.309	8, 1.393	2, 1.304
Absorption coefficient (mm^{-1})	0.769	0.674	1.015	0.858
F(000)	1400	1512	2376	1612
Crystal size (mm)	0.22 x 0.18 x 0.15	0.26 x 0.25 x 0.14	0.20 x 0.15 x 0.12	0.16 x 0.15 x 0.11
θ range for data collection (deg)	2.36 to 25.50	2.39 to 27.97	2.29 to 25.50	2.09 to 25.50
Limiting indices	-17<=h<=17, -13<=k<=13, -25<=l<=25	-27<=h<=27, -13<=k<=12, -21<=l<=21	-21<=h<=21, -19<=k<=19, -23<=l<=23	-14<=h<=14, -19<=k<=19, -23<=l<=23
Max. and min. transmission	0.8934 and 0.8490	0.8442 and 0.9115	0.8879 and 0.8227	0.9116 and 0.8750
Refinement method.	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6029 / 0 / 378	6728 / 0 / 414	5107 / 0 / 338	14283 / 1 / 881
Goodness-of-fit on S $(F^2)^a$	1.092	1.011	1.085	0.966
Final R indices [I>2ó(I)]	R1 = 0.0431, wR2 = 0.1144	R1 = 0.0243, wR2 = 0.0589	R1 = 0.0423, wR2 = 0.0958	R1 = 0.0691, wR2 = 0.1408
R indices (all data)	R1 = 0.0540, wR2 = 0.1275	R1 = 0.0283, wR2 = 0.0616	R1 = 0.0723, wR2 = 0.1105	R1 = 0.1533, wR2 = 0.1800
Largest diff peak and hole (e/$Å^3$)	0.791 and -0.872	0.361 and -0.179	0.448 and -0.518	0.637 and -0.406

$$R=\sum\left\|F_o\right|-\left|F_c\right\|\sum\left|F_o\right|;R_w=\left[\sum w\left(F_o^2-F_c^2\right)^2/\sum w\left(F_o^2\right)^2\right]^{1/2}$$

Table **2**. Selected Bond Lengths (Å) and Angles (deg) for the complexes

C1		**C2**		**C3**		**C4**	
bond	**length**	**bond**	**length**	**bond**	**length**	**bond**	**length**
Pd(1)-N(1)	2.033(3)	Pd(1)-N(1)	2.0555(19)	Cu(1)-N(1)	2.071(2)	Cu(1)-N(1)	2.066(5)
Pd(1)-N(2)	2.043(3)	Pd(1)-N(2)	2.042(2)	Cu(1)-N(2)	2.020(2)	Cu(1) - N(2)	2.062(6)
Pd(1)-Cl(1)	2.2669(10)	Pd(1)-Cl(2)	2.2568(9)	Cu(1)-Cl(1)	2.1815(10)	Cl(1)- Cu(1)	2.197(2)
Pd(1)-Cl(2)	2.2672(11)	Pd(1)-Cl(1)	2.2673(8)	Cu(1)-Cl(2)	2.1839(12)	Cl(2)-Cu(1)	2.203(2)
N(2)-C(15)	1.276(4)	C(1)- N(1)	1.280(3)	N(2)-C(17)	1.438(3)	N(2)-C(21)	1.442(9)
N(1)-C(17)	1.441(4)	N(1)- C(40)	1.454(3)	N(1)-C(25)	1.444(3)	C(25)-N(1)	1.290(8)
N(2)-C(25)	1.437(4)	C(17)- N(2)	1.451(3)	C(16)-N(2)	1.273(3)	C(42)-C(41)	1.553(12)
C(16)-N(1)	1.281(4)	C(10)- N(2)	1.277(3)	C(15)-N(1)	1.274(3)	C(25)-C(28)	1.495(10)
bond	**angle**	**bond**	**angle**	**bond**	**angle**	**bond**	**angle**
N(1)-Pd(1)-N(2)	81.01(10)	N(1)-Pd(1)-N(2)	80.44(8)	N(2)-Cu(1)-N(1)	80.76(9)	N(1)-Cu(1)-N(2)	79.7(2)
N(1)-Pd(1)-Cl(1)	92.96(8)	N(2)-Pd(1)- Cl(2)	174.60(8)	N(2)-Cu(1)-Cl(1)	142.66(8)	N(1)-Cu(1)-Cl(1)	172.33(18)
N(2)-Pd(1)-Cl(1)	173.38(8)	N(1)-Pd(1)-Cl(2)	94.17(6)	N(1)-Cu(1)-Cl(1)	96.65(7)	N(2)-Cu(1)-Cl(1)	93.21(16)
C(15)-N(1)- Pd(1)	112.2(2)	N(2)-Pd(1)-Cl(1)	94.80(7)	N(2)-Cu(1)-Cl(2)	97.95(7)	N(1)-Cu(1)-Cl(2)	92.07(17)
N(2)-Pd(1)-Cl(2)	93.37(8)	Cl(1)-Pd(1)-Cl(2)	90.60(4)	Cl(1)-Cu(1)-Cl(2)	104.37(5)	Cl(1)-Cu(1)-Cl(2)	95.09(9)
Cl(1)-Pd(1)-Cl(2)	92.60(4)	C(1)- N(1)- Pd(1)	112.05(16)	C(16)-N(2)-Cu(1)	113.44(18)	C(25)-N(1)-C(9)	119.5(6)

3.2 Polymerization of norbornene

In order to explore the effects of ligand environment and metal center on the catalytic performance, all the synthesized palladium and copper complexes were evaluated for polymerization of norbornene by using different lewis acid as co-catalyst under 35 ^{o}C. The detailed results were summarized in Table **3**. $AlEt_3$ and $B(C_6F_5)_3$ can not active palladium and copper complexes for norbornene polymerization, which is different from **α**-diimine nickel complexes by only using $B(C_6F_5)_3$ as co-catalyst for norbornene polymerization reported by our group.[38]

All the complexes demonstrated moderate activities ($1.07\text{-}3.03\times10^5 g_{polymer}/mol_{Mt}\cdot h$) in the presence of MAO. Palladium complexes exhibit higher activity than the corresponding copper complexes did. At the same time, large steric substituent in the aryl rings can effectively shield the axial plane of the central metal and suppress the side reaction of chain growth, so the catalytic behavior order was in **C2**, **C1**, **C4** and **C3**. The obtained PNBs were completely soluble in chlorobenzene, dichlorobenzene at room temperature, which indicated a low stereoregularity.

Table **3.** Norbornene polymerization

Run	Complex	Co-cat./[Mt]	Yield(%)	Activity (10^5 $g_{polymer}$/mol_{Mt} •h)
1	**C1**	$AlEt_3$/[Pd]=1000	0	0
2	**C1**	$B(C_6F_5)_3$/[Pd]=20	trace	trace
3	**C1**	MAO/[Pd]=1000	60.2	2.26
4	**C1**	MAO /$B(C_6F_5)_3$/[Pd]=1000/3/1	65.8	2.47
5	**C2**	$B(C_6F_5)_3$/[Pd]=20	trace	trace
6	**C2**	MAO/[Pd]=500	38.6	1.45
7	**C2**	MAO/[Pd]=1000	80.6	3.03
8	**C2**	MAO/[Pd]=2000	69.5	2.61
9	**C2**	MAO /$B(C_6F_5)_3$/[Pd]=1000/3/1	82.2	3.07
10	**C3**	$AlEt_3$/[Cu]=1000	0	0
11	**C3**	$B(C_6F_5)_3$/[Cu]=20	trace	trace
12	**C3**	MAO/[Cu]=1000	28.4	1.07
13	**C3**	MAO /$B(C_6F_5)_3$/[Cu]=1000/3/1	32.5	1.22
14	**C4**	$B(C_6F_5)_3$/[Cu]=20	trace	trace
15	**C4**	MAO/[Cu]=500	32.9	1.24
16	**C4**	MAO/[Cu]=1000	50.1	1.90
17	**C4**	MAO/[Cu]=2000	46.8	1.76
18	**C4**	MAO /$B(C_6F_5)_3$/[Cu]=1000/3/1	53.5	2.01

Reaction conditions: solvent :chlorobenzene, Mt(Pd or Cu) complex, 5×10^{-6} mol. total volume 15 mL, n[NB]/[Mt(Pd or Cu] = 2000, NB=2.35mL (0.0425mol/L),time = 30 min, polymerization temperature, 35 ^oC.

When three equivalents of boron compounds $B(C_6F_5)_3$ was added to **C1-C4** and MAO, the catalytic activities in norbornene polymerization reactions was enhanced, which suggested the electrophilicity of the metal center increased in favour of facilitating norbornene coordination and increasing in catalytic activity. For **C1**/MAO, activity from 2.26×10^5 $g_{polymer}/mol_{Pd}\cdot h$ to 2.47×10^5 $g_{polymer}/mol_{Pd}\cdot h$ when MAO/[Pd]=1000 and MAO/B$(C_6F_5)_3$/[Pd]=1000/3/1 used respectively were observed.

3.3 **Copolymerization with Norbornene and 2-butyloxymethylene norbornene**

Palladium complex **C2** was used to study the copolymerization of norbornene (NB) and 2-butyloxymethylene norbornene (BN) and the results were shown in Table **4**. The catalytic systems maintained a moderate activity even if polymerization conditions changed. The M_W of the copolymers obtained by complexes **C2**/MAO systems were over 100kg mol^{-1} and decreased with increasing the content of BN in the copolymer. Although the PDIs of the obtained polymers were 2.28 to 3.88, which appear as a single modal in the GPC curves (**Fig.S9** in ESI) indicated the copolymerization occured at single active sites and the products were true copolymers rather than the blends of homopolymers. The fraction of BN in copolymer could reach up to 9.8-62.1% by controlling monomer feed ratio from 10-80%. The achieved vinyl-addition type poly(NB-co-BN) copolymers displayed high thermal stability and were soluble in common organic solvents, such as $CHCl_3$ and THF.

Table **4.** NB/BN copolymerization with **C2**/MAO [a]

Run	BN (mol%)	Yield (%)	Activity[b]	M_w (g/mol)[c]	M_w/M_n[b]	BN incorp. (%)
1	10	78.6	1.1×10^5	5.23×10^5	2.28	9.8
2	30	75	1.07×10^5	4.01×10^5	3.42	22.4
3	50	72	1.02×10^5	3.21×10^5	3.63	37.5
4	60	70.2	9.87×10^4	2.96×10^5	3.88	43.6
5	80	65.8	8.99×10^4	2.62×10^5	3.76	62.1
6	100	60.5	8.06×10^4	2.21×10^5	3.26	100

[a] Reaction conditions: solvent: chlorobenzene, n{[NB] +[BN]}= 0.01 mol; **C2**:5×10^{-6} mol(3.65×10^{-3} g), total volume 15 mL. n{[NB]+[BN]}/MAO/[C2]=2000/1000/1; polymerization temperature, 35 °C, time=30 min.

[b] In units of $g_{polymer}$/molPd•h

[c]Determined by GPC (**Fig.S9**), solvent: 1,2,4-Trichlorobenzene; temperature:150°C;

calibration with polystyrene standards.

3.4 Microstructure of copolymers

The microstructures of the obtained poly(NB-co-BN) copolymers were characterized by NMR and FTIR spectra. The ^{1}H NMR data of the copolymers containing different contents of BN were collected in deuterated chloroform ($CDCl_3$) at room temperature (Fig**. 5**). No resonances displayed from 5.0–6.0 ppm in the ^{1}H NMR spectra, which indicated the presence of ring-opening metathesis polymerization (ROMP) polymer structures. The incorporations of BN into the copolymers were calculated through the signal intensity of $–CH_2OCH_2–$ protons at 3.69~3.78 ppm. The ^{13}C NMR spectrum (Fig**. 6**) also further confirmed that the obtained polymers were vinyl-type poly(NB-co-BN). The ^{13}C NMR spectrum showed the main four groups of resonances: (53.4, 51.8, 47.5), (42.3, 39.2, 37.6, 36.5), (35.1), and (30.4, 29.3) ppm, which could be attributed to the backbone carbon (C2/C2$^/$, C3/C3$^/$), bridge head carbon (C1/C1$^/$, C4/C4$^/$), bridge carbons (C7/C7$^/$) and (C5/C5$^/$, C6/C6$^/$) of vinyl-type polymer structures of norbornene, respectively. The resonances of methenes appeared at 61.9–62.4 ppm for $–CH_2OCH_2–$ carbons. C=C double bond (120 ppm) characteristic peaks owing to ROMP polymer stuctures were absent from the spectra, which implied that the copolymerization of NB and BN catalyzed by **C2**/MAO via a vinyl-addition polymerization.

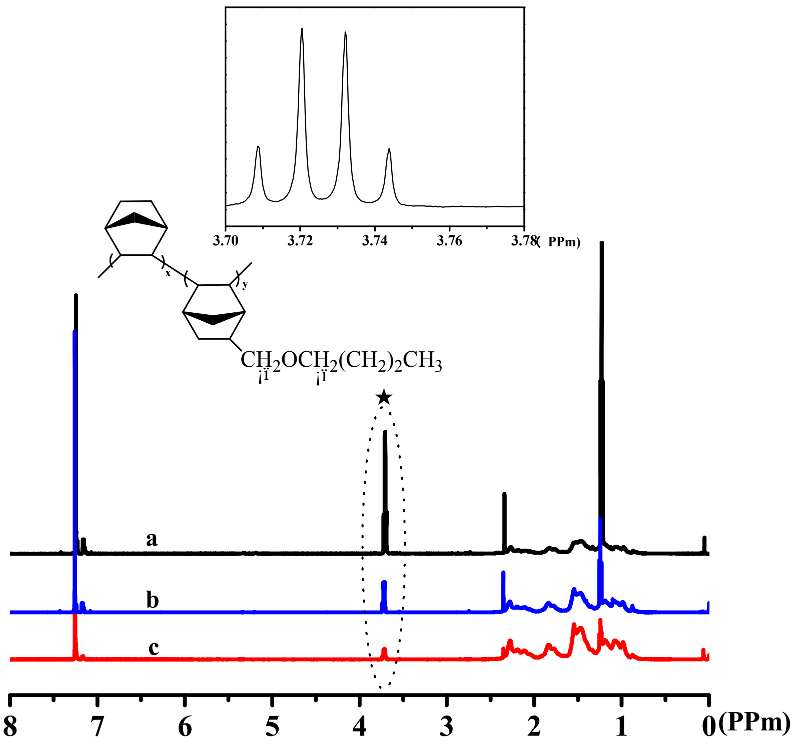


Fig. **5.** ^{1}H NMR spectrum of copolymer containing (a) 62.1, (b) 22.4, (c) 9.8 mol% BN content recorded in CDC1$_3$ at room temperature by using **C2**/MAO system.

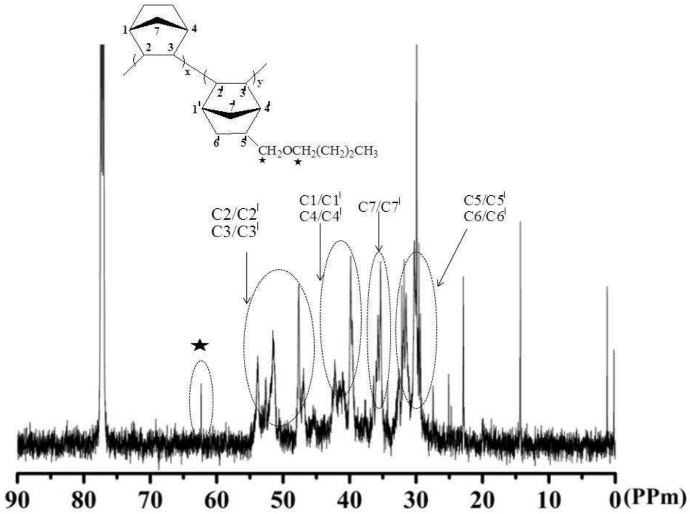


Fig. **6.** ^{13}C NMR spectrum of copolymer containing 62.1 mol% BN content recorded in CDC1$_3$ at room temperature by using **C2**/MAO system.

The FTIR spectra of the poly(NB-co-BN) copolymers were shown in Fig. **7**. No vibration bands of carbon-carbon double bond at 1620-1680 cm^{-1} and 960cm^{-1} in the spectra, which suggesting that NB was copolymerized with BN in a vinyl-type rather than ROMP mechanism. Moreover, we could find that the characteristic absorption signal of the ether group (C-O-C) at 1105 cm^{-1} in the FTIR spectra signified the incorporation of BN. The absorption strength of the ether group (C-O-C) group increased with an increase of the BN content in the co-monomer feed.

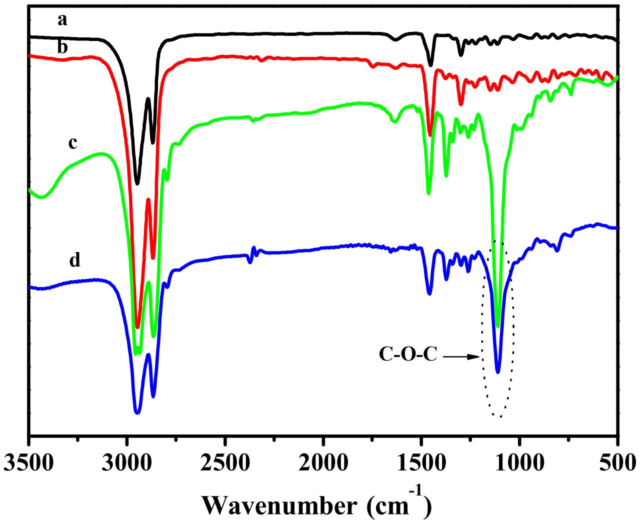


Fig. **7.** FTIR spectra of poly(NB-co-BN) with (a) 0, (b) 0, (c) 100, (d) 37.5mol% BN incorporation ratios. (a), (c), (d) obtained by **C2**/MAO system, (b) obtained by **C4**/MAO system.

3.5 TGA analyses of polymers

TGA analyses indicated that the copolymers, obtained by the **C2**/MAO catalytic systems, exhibited good thermo stability under nitrogen. The TGA curves of the copolymers were shown in Fig. **8**. Thermogravimetric analyses showed that all these polymers were stable up to 410 °C and beyond that they started to decompose.

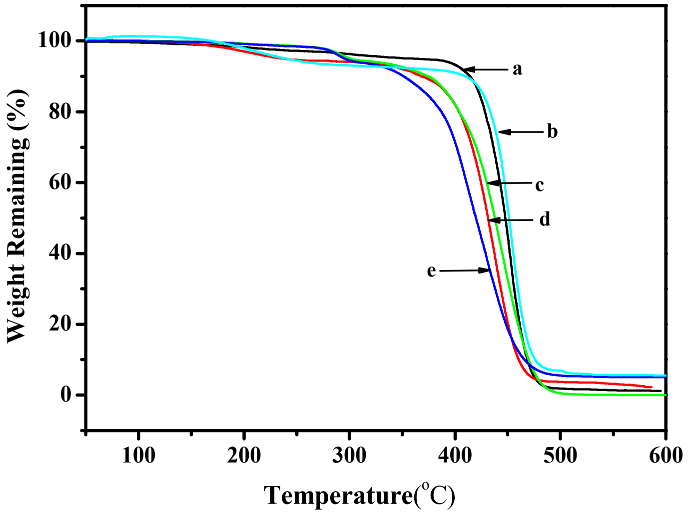


Fig. **8.** TGA curves of copolymer containing (a) 9.8, (b) 22.4, (c) 37.5 (d) 43.6, (e) 62.1 mol% BN content by using **C2**/MAO system

3.6 WXRD analyses of copolymers

Partial information on the conformation of the copolymers samples, achieved by palladium complex **C2,** was obtained by means of wide-angle X-ray diffraction (WAXD). As seen in Fig.**9**, two wide and weak signals at a diffraction angle 2θ=10.36 and 18.64 were observed, which were characteristic peaks for noncrystalline or lower crystalline poly(NB-co-BN).[40-41] We believed that the poly(NB-co-BN) obtained with this catalyst contained limited range of orderly segments.

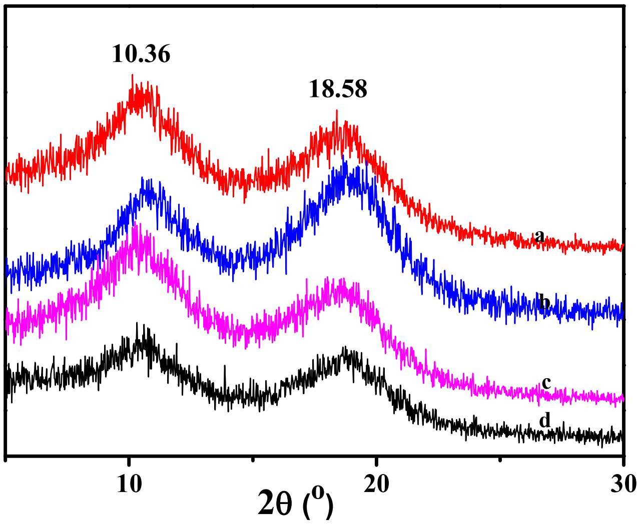


Fig. **9. W**AXD curves of poly (NB-co-BN): (a) 0, (b) 37.5, (c) 43.6 (d) 62.1 mol% BN content by using **C2**/MAO system

4. Conclusions

Several palladium(II) and copper(II) chloride complexes bearing bulky α-diimine ligands were successfully synthesized and characterized. Activation of these complexes with MAO, all these complexes displayed catalytic activities up to 10^5 $g_{polymer}/mol_{Mt}$•h for norbornene vinyl-addition polymerization. The catalytic activities relied on the type of metal and the ligand environment. Generally, the palladium(II) complexes showed better catalytic activities than copper(II) catalysts did. Catalytic activities can reach to 1.1×10^5 $g_{polymer}/mol_{Pd}$•h when **C2** as catalyst precursor for the copolymerization of norbornene and 2-butyloxymethylene norbornene. The fraction of BN in copolymer could reach up to 9.8-62.1% by controlling monomer feed ratios from 10-80%.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51463014 and 21164006).

Supplementary material

Crystallographic data for the structural analysis were deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 1436570，1436571，1436572 and 1436573 for **C1**, **C2**, **C3** and **C4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.ukor. http://www.ccdc.cam.ac.uk). ^{1}H NMR and ^{13}C NMR spectra of C1,C2,C3 and C4 and GPC curves of the poly (NB-co-BN) with different BN molar ratios(%) are shown as **Fig.S1-Fig.S9** in Electronic Supplementary Material (ESI).

References

1 C. Mast, M. Krieger, K. Dehnicke, A. Greineret, Macromol. Rapid Commun., 1999, 20, 232-235.

2 K. Vijayakrishna, S. Padmanabhan, T. Kannan, D. Dakshinamoorthy, Polymer bulletin., 2012, 68(3): 635-645.

3 P. Hu, Z. J. Yao, J. Q. Wang, G. X. Jin, Organometallics, 2011, 30, 4935-4940.

4 Y. L. Qiao and G. X. Jin, Organometallics, 2013, 32, 1932-1937.

5 D. A. Barnes, G. M. Benedikt, B. L. Goodall, S. S. Huang, H. A. Kalamarides, S.Lenhard, L. H. III.McIntosh, K. T.Selvy, R. A. Shick and L.F. Rhodes, Macromolecules., 2003, 36, 2623-2632.

6 F. Blank, J. K. Vieth, J. Ruiz, V. Rodríguez, C. Janiak, Journal of Organometallic Chemistry, 2011, 696,473-487.

7 U. Peucker, W. Heitz, Macromol. Rapid Commun., 1998, 19, 159-162.

8 O. Nishizawa, H. Misaka, T. Kakuchi, T. Satoh, J, Polym. Sci., Part A: Polym. Chem., 2008, 46,1185-1191.

9 W. Kaminsky, A. Bark, M. Arndt, Makromolekulare Chemie. Macromolecular

Symposia. 1991, 47(1): 83-93.

10 B. L. Goodall, L. H. McIntosh and L. F. Rhodes, Macromol. Symp., 1995, 89, 421-432.

11 K. H. Park, R. J. Twieg, R. Ravikiran, L. F. Rhodes, R. A. Shick, D. Yankelevich,A.Knoesen, Macromolecules ., 2004,37,5163-5178.

12 T. Hoskins, W. J. Chung, A. Agrawal, J. Ludovice, C. L. Henderson, L. D. Seger,L. F. Rhodes, R. A. Shick, Macromolecules., 2004,37,4512-4518.

13 H. Ito, H. D. Truong, L. F. Rhodes, C. Chang, L. J. Langsdorf, H. A. Sidaway, K. Maeda, S. Sumida, J. Photopolym. Sci. Technol., 2004,17 ,609-614.

14 X. Q. Wu, H. A. Reed, Y. Wang, L. F. Rhodes, E. Elce, R. Ravikiran, R. A. Shick,C. L. Henderson, S. A. B. Allen, P. A. Kohl, J. Electrochem. Soc., 2003,150, 2 05-213.

15 N. R. Grove, P. A. Kohl, S. A. B. Allen, S. Jayaraman, R. Shick, J. Polym. Sci.: Part B: Polym. Phys., 1999, 37, 3003-3008.

16 L. Y. Wang, Y. F. Li, F. M. Zhu, Q. Wu, Euro Polym J., 2006,42, 322-327.

17 K. Ogata, A. Watanabe, T. Yunokuchi, A. Toyota, Inorg Chem Commun., 2008, 11, 215-219.

18 T. Hu, Y. G. Li, Y. S. Li, N. H. Hu, J Mol Catal A: Chem.,2006, 253, 155-164.

19 L. K. Johnson,C. M. Killian, M. Brookhart, J. Am. Chem. Soc. 1995, 117, 6414-6415.

20 C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart, J. Am. Chem. Soc. 1996, 118, 11664-11665.

21 A. S. Abu-Surrah, M. Kettunen, K. Lappalainen, U. Piironen, M. Klinga, M. Leskela, Polyhedron., 2002, 21, 27-31.

22 Z. Guan, P. M. Cotts, E. F. McCord, S. Mclain, Science, 1999,283,2059-2062.

23 W. Zhang, W. H. Sun, B. Wu, S. Zhang, H. Ma, Y. Li, J. Chen, P.Hao, J. Organomet. Chem., 2006,691, 4759-4767.

24 J. H. Groen, G. J. P. Delis, P. W. N. M. van Leeuwen, K. Vrieze,Organometallics, 1997,16, 68-77.

25 J. G. P. Delis, P. G. Aubel, K. Vrieze, P. W. N. M. van Leeuwen, N.Veldman, A.

L. Spek, F. J. R. van Neer, Organometallics, 1997, 16, 2948-2957.

26 D. M. Shin, S. U. Son, B. K. Hong, Y. K. Chung, S. H. Chun, J.Mol.Cat. A., 2004, 210, 35-46.

27 B. L. Small, M. Brookhart, A. M. A Bennett, J. Am. Chem. Soc.1998, 120, 4049-4050.

28 B. A.Rodriguez, M.Delferro, T. J Marks, Organometallics, 2008, 27, 2166-2168.

29 H. Wu, Y. Liu, S. Peng, S. Liu, Eur J Inorg Chem, 2003, 2003, 3152-3159.

30 H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang, W. H. Sun, Organometallics, 2011, 30, 2418-2424.

31 C. S. Popeney, C. M. Levins, Z. B. Guan, Organometallics, 2011, 30, 2432-2452.

32 D. P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White, M. Brookhart, Macromolecules, 2000, 33, 2320-2334.

33 M. M .Wegner, A. K. Ott, B. Rieger, Macromolecules, 2010, 43,3624−3633.

34 C. S. Popeney, Z. B. Guan, Macromolecules, 2010, 43, 4091-4097.

35 F. S. Liu, H. B. Hu, Y. Xu, L. H. Guo, S. B. Zai, K. M. Song, H. Y. Gao, L. Zhang, F. M. Zhu, Q. Wu, Macromolecules, 2009, 42, 7789-7796.

36 D. H.Leung, J. W.Ziller, Z. B.Guan, J. Am. Chem. Soc.2008,130, 7538-7539.

37 J. W. Tian, X. H. He, J.Y. Liu, X. D. Deng, D. F. Chen, RSC Advances, 2015, 5, 61851-61860.

38 P. Huo, W. Y. Liu, X. H. He, H. M. Wang , Y. W. Chen, Organometallics, 2013, 32, 2291-229.

39 V. C. Gibson, A. Tomov, D. F. Wass, A. J. White, D. J. Williams, Dalton Transactions, 2002, 11, 2261-2262.

40 G. Ricci, A. Boglia, A. C Boccia, L. Zetta, A.Famulari, S. V. Meille, Macromolecules, 2008, 41, 3109-3113.

41 G. Tang, Y. Lin, G. Jin, J Polym Sci A.,2008, 46,489-500.