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Synthesis of nickel and palladium complexes with diarylamido-based unsymmetrical pincer ligands and application for norbornene polymerization†

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A set of diarylamido-based unsymmetrical [PNN^{ox}] pincer ligands containing a chiral oxazoline ring have been synthesized and their nickel and palladium complexes [(2-PPh$_2$(R^1)ArN(R^1)Ar-2-(R)oxazoline)MCl] (R^1 = 4-H, R = (*S*)-4-^{i}Pr, M = Pd (**Pd1**); R^1 = 4-H, R = (*S*)-4-Bn, M = Pd (**Pd2**); R^1 = 4-H, R = (*S*)-4-Ph, M = Pd (**Pd3**); R^1 = 4-Me, R = (*S*)-4-Bn, M = Pd (**Pd4**); R^1 = 4-Me, R = (*S*)-4-Ph, M = Pd (**Pd5**); R^1 = 4-H, R = 4-Me$_2$, M = Pd (**Pd6**); R^1 = 4-H, R = Benzo[*d*]-, M = Pd (**Pd7**); R^1 = 4-H, R = (*S*)-4-Bn, M = Ni (**Ni1**); R^1 = 4-H, R = (*S*)-4-Ph, M = Ni (**Ni2**); R^1 = 4-Me, R = (*S*)-4-Bn, M = Ni (**Ni3**); R^1 = 4-Me, R = (*S*)-4-Ph, M = Pd (**Ni4**)) were tested to show high catalytic activities for polymerization of norbornene. After activation of methylaluminoxane (MAO), all the nickel and palladium complexes could catalyze the polymerization of norbornene to yield vinyl-type polymers with activities up to 40.3 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}. The copolymerization of norbornene with functional norbornene comonomers was also investigated by catalyst **Pd2**, accompanied by decreased catalytic activity and low incorporation of functional comonomers.

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Introduction

Homogeneous late-transition metal catalysts for coordination–insertion polymerization of olefins have attracted extensive investigation over the last few decades.[1] As representative pre-catalysts, nickel and palladium complexes bearing bulky α-diimine,[2] salicylaldiminato[3] and phosphine-sulfonate[1g] ligands have been applied to the catalysis of ethylene polymerization and copolymerization with polar monomers to obtain polymers with diverse micro-architectures and tailored physical properties. Some nickel and palladium complexes have also proved to be amongst the most efficient catalysts for the vinyl-type polymerization of norbornene with high activities.[4,5] Of the nickel and palladium pre-catalysts reported for norbornene polymerization, most are involved in bidentate neutral or monoanionic ligand chelating complexes.[4] Nickel and palladium complexes based on unsymmetrical and symmetrical tridentate [NNX] (X = N, P, S), [ONX] (X = C, N, P) ligands have also been designed and extensively tested for the polymerization of norbornene,[5] however, the tridentate "pincer" type ligands and their chelated pre-catalysts have rarely been reported.[5b,j,k] Wu *et al.* reported a series of unsymmetrical tridentate pincer [NNS] ligands, and the corresponding nickel and palladium complexes have proved efficient catalysts for norbornene polymerization.[5b] Recently, Li *et al.* described Ni and Pd complexes bearing chiral C_2-symmetrical bis(oxazoline) [N^{ox}NN^{ox}] pincer ligands as exhibiting unique catalytic performance in norbornene polymerization, even with extremely high activities in the presence of air and water.[5j,k]

Generally, ligands chelated to metal centres in homogeneous catalysis systems have a remarkable influence on the catalytic properties and the microstructures of the resultant products, thus intensive efforts have been paid to the ligands with new architectures. Tridentate pincer ligands represent a ligand architecture in transition-metal chemistry, particularly from the point of view of their wide applications in catalysis.[6] Due to the convenient modularity of the diarylamido scaffold, derived pincer ligands, including [PNP],[7] [NNN][8] and [PNN][9] ligands, have been reported. As a very useful supporting ligand for metals across the periodic table, the diarylamino-based [PNP] ligand class (Fig. 1A) has revealed species with unusual structures or reactivity.[10,11] The [PNP] ligands have also proved versatile in olefin polymerization, and their rare-earth complexes could serve as excellent catalysts for the polymerization of both isoprene and butadiene.[12] The C_2-symmetric tridentate bis-(oxazolinylphenyl)amine [N^{ox}NN^{ox}] ligand class (Fig. 1B) is another unique scaffold which has been extensively studied in diverse applications, of which the field of asymmetric reac-

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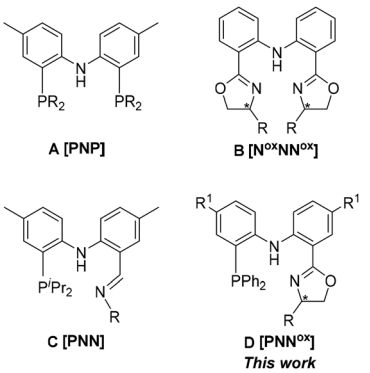


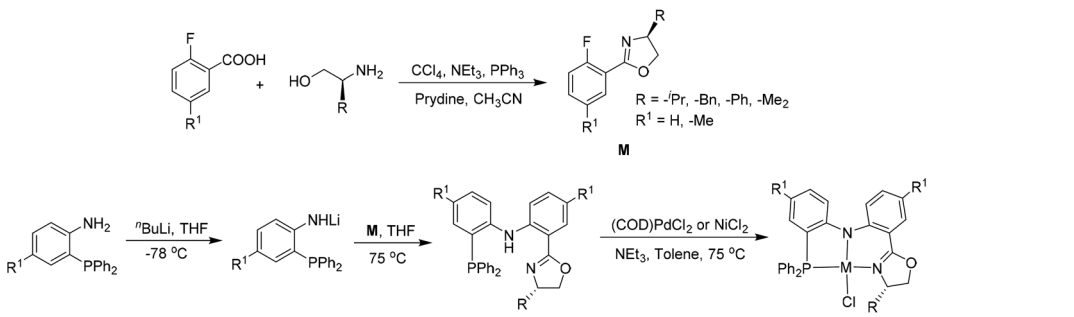
Fig. 1 Typical diarylamido pincer ligands for transition-metal complexes.

tions has highlighted their versatility and tunability.[13] The polymerization of isoprene and norbornene catalysed by chiral bis-(oxazolinylphenyl)amine ligated metal complexes has recently been reported.[5j,k,14] As we are interested in designing new pincer ligands, we combined these two special skeletons to obtain a series of new unsymmetrical [PNN^{ox}] pincer ligands (Fig. 1D), which can be seen as half the bis(phosphinophenyl)amido [PNP] ligand and half the bis-(oxazolinylphenyl)amine [N^{ox}NN^{ox}] ligand. Previously, Ozerov *et al.* reported a similar diarylamido-based unsymmetrical [PNN] pincer ligand (Fig. 1C) and tested the electronic properties of their Ni, Pd, Pt and Rh complexes.[9b] Herein, the tunable oxazoline-ring skeleton can provide different electronic effects and novel chiral surroundings to metal centres which may impart special catalytic performance and promote catalytic stereoselectivity of the ligated complexes in some circumstances.

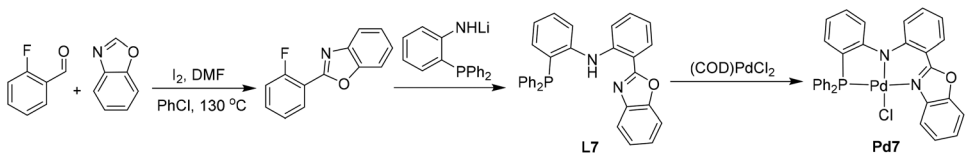
We report a set of new diarylamido-based unsymmetrical [PNN^{ox}] pincer ligands containing a chiral oxazoline-ring and their corresponding nickel and palladium complexes. Upon activation with MAO, these palladium complexes catalyse the vinyl-type polymerization of norbornene to yield insoluble polymers with high activities up to 40.3 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}. Meanwhile, the analogous nickel complexes exhibited relatively lower activities, and soluble high-molecular-weight polymers with moderate molecular weight distributions are obtained. The copolymerization of norbornene with functional norbornene comonomers is also studied.

Results and discussion

The unsymmetrical [PNN^{ox}] pincer ligands with different chiral oxazoline rings were synthesized as described in Scheme 1. The one-pot condensation of 2-fluorobenzoic acid and substituted amino alcohols afforded the fluorophenyloxazolines (**M**) with good yield.[15] The subsequent nucleophilic aromatic substitution of fluorine in **M** by salt elimination with the corresponding 2-phosphinoarylamino lithium salts in THF gave the desired tridentate [PNN^{ox}] pincer ligands. The achiral ligands **L6** and **L7** were also synthesized for comparison, and the benzoxazole-containing ligand **L7** was synthesized in a different way according to Scheme 2. After purification by column chromatography on silica gel, all the tridentate [PNN^{ox}] pincer ligands were obtained as yellow solids except **L1** which was a yellow sticky oil. Various analysis methods,



Scheme 1 Synthesis of unsymmetrical pincer ligands and their palladium and nickel complexes.



Scheme 2 Synthesis of achiral ligands **L7** and its palladium complex **Pd7**.

including ^{1}H and ^{13}C NMR spectra and elemental analysis, proved the formation and purity of the ligands **L1–L7**, such as the new –N*H* signal at 10.50 ppm in the proton spectrum resonance spectroscopy of **L1** indicating the coupling of the reactants. Previous studies concerning the synthesis of anilido-oxazolines always involved the Pd-catalysed aryl amination,[16] and the approach involving lithium salt-elimination described here provides an alternative route to prepare these analogous compounds.

Having the unsymmetrical tridentate [PNN^{ox}] pincer ligands in our hands, we tried to synthesize their corresponding nickel and palladium complexes. According to previous reports, the [PNN^{ox}] pincer ligands in this study are ideally suitable to support various square-planer complexes of the general formula (PNN^{ox})MCl (M = Ni, Pd).[5] Firstly, the treatments of the lithium salts of the ligands with (COD)$PdCl_2$ in THF at RT or 70 °C gave dark red powders, however, impurities were observed in both the cases determined by ^{1}H NMR spectroscopy. However, the side reactions could be suppressed using toluene as solvent enabling pure palladium complexes to be obtained. In addition, the direct reactions of the neutral [PNN^{ox}] pincer ligands with (COD)$PdCl_2$ in toluene at 70 °C could also afford the desired palladium complexes in pure form, and the addition of a base such as NEt_3 was necessary to remove the HCl by-product during the formation of (PNN^{ox})PdCl, providing an optimal pathway to synthesize these analogous complexes. Similarly, the reaction of selected chiral [PNN^{ox}] pincer ligands with anhydrous $NiCl_2$ in the presence of NEt_3 produced the corresponding pure (PNN^{ox})NiCl (Scheme 1). All the nickel and palladium complexes were fully characterized by ^{1}H, ^{13}C NMR spectroscopy. However, due to difficulties in complete solvent removal from the complexes, we could not obtain satisfactory elemental analysis data. The disappearance of the –N*H* signals at around 10–11 ppm in the ^{1}H NMR spectra indicated the formation of the coordinated complexes. All the resulting nickel and palladium complexes are soluble in common organic solvents such as toluene and dichloromethane, and stable in oxygen and moisture-containing environments.

Single crystals of the complexes **Pd1**, **Pd2**, **Pd6** and **Pd7** suitable for X-ray structure determination were obtained from slow evaporation of their CH_2Cl_2/hexane solutions at room temperature. The corresponding ORTEP diagrams are presented in Fig. 2–5 along with selected bond lengths and bond angles, respectively. Molecular structure analyses revealed that all the palladium complexes adopt an approximately square-planar geometry around the metal centre with coordinated P, N, N and a chloride atom. Due to the similar structures and coordination environments, the palladium complexes resemble each other in bond lengths and bond angles, nevertheless, the role of the chiral substituents cannot be ignored. The bond lengths of Pd(1)–N(2) are 2.0885(19) Å (**Pd1**) and 2.063(3) Å (**Pd2**), are not as much as those in achiral **Pd6** (2.095(2) Å) and **Pd7** (2.109(3) Å). The chiral substituents have a significant influence on the bond angles while involving the chloride atom. The N(2)–Pd(1)–Cl(1) angles in **Pd1** and **Pd2** are 94.08(6)° and 92.36(9)°, smaller than the corresponding angles in **Pd6** and **Pd7** (96.68(7)° and 97.62(11)°, respectively). The N(1)–Pd(1)–Cl(1) angles are 177.50(5)° (**Pd1**) and 178.14(8)° (**Pd2**) are notably larger than the corresponding angles in **Pd6** (173.56(6)°) and **Pd7** (173.16(9)°), indicating that the metal centre and the coordinated atoms in chiral palladium com-

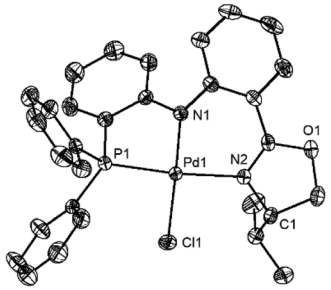


Fig. 2 Molecular structure of **Pd1** (thermal ellipsoids at the 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.0166(19), Pd(1)–N(2) 2.0885(19), Pd(1)–P(1) 2.2134(11), Pd(1)–Cl(1) 2.3121(12); N(1)–Pd(1)–N(2) 87.68(7), N(1)–Pd(1)–P(1) 84.18(6), N(2)–Pd(1)–P(1) 170.35(5), N(1)–Pd(1)–Cl(1) 177.50(5), N(2)–Pd(1)–Cl(1) 94.08(6), P(1)–Pd(1)–Cl(1) 94.21(3).

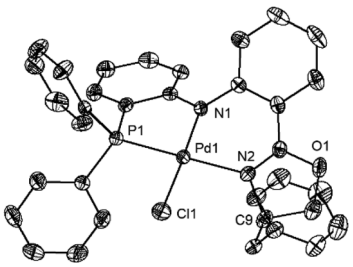


Fig. 3 Molecular structure of **Pd2** (thermal ellipsoids at the 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.022(3), Pd(1)–N(2) 2.063(3), Pd(1)–P(1) 2.213(2), Pd(1)–Cl(1) 2.312(2); N(1)–Pd(1)–N(2) 89.28(11), N(1)–Pd(1)–P(1) 84.84(8), N(2)–Pd(1)–P(1) 171.72(8), N(1)–Pd(1)–Cl(1) 178.14(8), N(2)–Pd(1)–Cl(1) 92.36(9), P(1)–Pd(1)–Cl(1) 93.61(4).

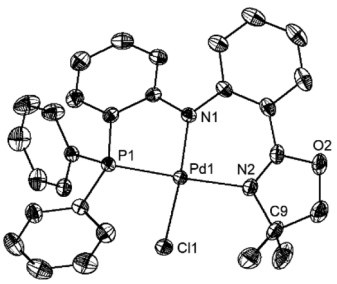


Fig. 4 Molecular structure of **Pd6** (thermal ellipsoids at the 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.010(2), Pd(1)–N(2) 2.095(2), Pd(1)–P(1) 2.1977(10), Pd(1)–Cl(1) 2.3123(10); N(1)–Pd(1)–N(2) 88.73(9), N(1)–Pd(1)–P(1) 84.61(7), N(1)–Pd(1)–P(1) 166.98(6), N(1)–Pd(1)–Cl(1) 173.56(6), N(2)–Pd(1)–Cl(1) 96.68(7), P(1)–Pd(1)–Cl(1) 90.74(5).

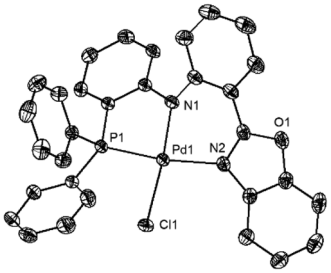


Fig. 5 Molecular structure of **Pd7** (thermal ellipsoids at the 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.032(3), Pd(1)–N(2) 2.109(3), Pd(1)–P(1) 2.1919(15), Pd(1)–Cl(1) 2.3118(17); N(1)–Pd(1)–N(2) 89.06(14), N(1)–Pd(1)–P(1) 83.56(11), N(1)–Pd(1)–P(1) 172.12(10), N(1)–Pd(1)–Cl(1) 173.16(9), N(2)–Pd(1)–Cl(1) 97.62(11), P(1)–Pd(1)–Cl(1) 89.84(6).

plexes are more approaching one perfect square-plane. Due to the different coordination effects of P and N atoms in the unsymmetrical palladium complexes,[9b] longer Pd–N (oxazoline) (2.063(3)–2.109(3) Å) and shorter Pd–P (2.1919(15)–2.2134(11) Å) bond lengths are found compared to those in related symmetrical [$N^{ox}NN^{ox}$]PdCl (around 1.996(6) Å) and [PNP]PdCl (2.3010(18) Å).[5j,17] The remaining parameters are unexceptional with typical ligand–metal distances and angles as previously reported.

Norbornene polymerization by unsymmetrical palladium and nickel complexes

Under the co-activation of MAO, all the palladium complexes could catalyse the polymerization of norbornene efficiently to afford insoluble vinyl-type polymers, and the corresponding nickel complexes exhibited poor catalytic performances. To clarify the optimal reaction parameters in the polymerization, **Pd2** was studied in detail as catalytic precursor, and the representative results are collected in Table 1. As an essential part for coordination polymerization, the cocatalyst *ca.* methylaluminoxane (MAO) plays an important role to form an active species, to maintain active catalyst precursors as well as to form catalytically active cation–anion ion pairs.[18] In the absence of MAO, it was unsurprising that the chloride complex of **Pd2** was inactive for the polymerization of norbornene due to the lack of a cationic M^+–C centre for initiation and propagation.[18a] The catalytic activity of **Pd2** increased sharply from 2.2 to 13.0 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1} along with the [Al]/[Pd] from 3000 increasing to 5000 (entries 2 and 3 in Table 1). When the ratio of [Al]/[Pd] reached 7000, the highest catalytic ability, 26.5 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}, was obtained (entry 4 in Table 1). The extreme excess of MAO needed in the polymerization might be mainly attributed to scavenging impurities and regenerating the active species deactivated by transformation/elimination in the system.[18,19] According to previous reports, the polymerization of norbornene possibly proceeded through a bimetallic mechanism (Scheme S1†).[5j,18] When MAO was replaced by a borate *ca.* ([Ph_3C][$B(C_6F_5)_4$] or [$PhMe_2NH$][$B(C_6F_5)_4$] and a borane $B(C_6F_5)_3$) as a co-catalyst, no polymers were obtained,[5j] even at a prolonged polymerization time of 600 minutes (entry 11 in Table 1). We reason that the formation of active cationic species for polymerization does not operate due to the absence of an initial M–C bond in **Pd2**.[18a,20] The reaction temperature is another significant parameter to control the polymerization process besides the usage of MAO. When the norbornene polymerization was conducted by the **Pd2**/MAO system at 0 °C, only a 12.3% yield of PNB was obtained in 10 minutes with a catalytic activity of 4.9 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1} (entry 6 in Table 1). Notable increases in polymer yield and catalytic activity were observed when the temperature increased to 25 °C, and the activity soared to 26.5 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1} (entry 4 in Table 1). However, when the temperature exceeded 80 °C, a significant decrease *ca.* 50% in catalytic activity compared to that at 25 °C was found, implying the importance of an appropriate polymerization temperature for this **Pd2**/MAO system. It is not difficult to understand that the yields of PNB increased along with the polymerization time, while the catalytic activities of **Pd2** decreased (from 40.3 to 14.3 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}) due to the viscosity of the converted PNB slowing down the catalytic rate. The obtained polymers were insoluble in ordinary solvents, even in boiling 1,2-dichlorobenzene. The insoluble polymers prevented us from obtaining detailed information of the molecular weight by high temperature gel-permeation chromatography (HT-GPC) and chemical structures by NMR spectroscopy. Characterization of all the obtained insoluble PNBs by IR spectroscopy showed very similar signals, and no signals at 1620–1680, 966 and 755 cm^{-1} indicating the polymers were of the vinyl-addition type (Fig. S37†).

Table 1 Results of norbornene polymerization with **Pd2**/cocatalysts systems[a]

Entry	T (°C)	co-Cat.	[Al]/[Pd]	t (min)	Yield (%)	Activity[c]
1	25	MAO	1000	10	Trace	—
2	25	MAO	3000	10	5.4	2.2
3	25	MAO	5000	10	32.4	13.0
4	25	MAO	7000	10	66.2	26.5
5	25	MAO	10 000	10	56.5	22.6
6	0	MAO	7000	10	12.3	4.9
7	50	MAO	7000	10	65.8	26.3
8	80	MAO	7000	10	35.2	14.1
9	25	MAO	7000	5	50.4	40.3
10	25	MAO	7000	20	71.5	14.3
11	25	A/B/C[b]	10	600	—	—

[a] Polymerization conditions: Complex, 1.5 μmol, toluene, V_{total} 10 mL, norbornene 1 g. [b] Activator: [Ph_3C][$B(C_6F_5)_4$] (A), [$PhMe_2NH$][$B(C_6F_5)_4$] (B), borane $B(C_6F_5)_3$ (C). [c] In units of 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}.

The nickel and palladium complexes bearing different unsymmetrical [PNN^{ox}] pincer ligands with various chiral and achiral substituents and skeletons have been applied in norbornene polymerization to study the structure–reactivity relationships. The norbornene polymerization results of **Pd1**–**Pd7** and **Ni1**–**Ni4** are presented in Table 2. Under the optimal conditions established by the **Pd2**/MAO system, all the palladium complexes showed high catalytic activity for the polymer-

Table 2 Results of norbornene polymerization with palladium and nickel complexes/cocatalysts systems[a]

Entry	Cat.	R^1–R	co-Cat.	[Al]/[Pd]	*t*/min	Yield/%	Activity[b]	M_n[c]/ × 10^5	M_w/M_n [c]
1	**Pd1**	H–^{i}Pr	MAO	7000	10	86.2	34.5		
2	**Pd2**	H–Bn	MAO	7000	10	66.2	26.5		
3	**Pd3**	H–Ph	MAO	7000	10	43.1	17.2		
4	**Pd4**	Me–Bn	MAO	7000	10	28.6	11.4		
5	**Pd5**	Me–Ph	MAO	7000	10	6.8	2.7		
6	**Pd6**	H–Me_2	MAO	7000	10	11.2	4.5		
7	**Pd7**	H–benzoxazole	MAO	7000	10	22.6	9.0		
8	**Ni1**	H–Bn	MAO	7000	60	22.2	1.5	0.82	1.84
9	**Ni2**	H–Ph	MAO	7000	720	21.8	0.12	1.44	2.16
10	**Ni3**	Me–Bn	MAO	7000	270	9.2	0.14	1.24	1.62
11	**Ni4**	Me-Ph	MAO	7000	300	14.2	0.19	1.56	1.56

[a] Polymerization conditions: Complex, 1.5 μmol, toluene, V_{total} 10 mL, norbornene 1 g, 25 °C. [b] In units of 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}. [c] Determined by GPC against polystyrene standard at 150 °C in 1,2,4-trichlorobenzene.

ization of norbornene to give insoluble polymers. When the substituent R^1 was H, the complex **Pd1** showed the highest activity of 34.5 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1} (entry 1 in Table 2), and the catalytic activity decreased in the order of **Pd1** > **Pd2** > **Pd3** > **Pd7** > **Pd6**. The steric hindrance and electronic effect of the ligand have a crucial influence on the catalytic performance. The relatively lower activity of achiral **Pd6** with two methyl groups substituted on the oxazoline ring showed the negative effect of a bulky hindrance. The catalytic activity order of **Pd2** > **Pd3** > **Pd7** clearly proves that the conjugated structures or electron-donating substituents were unfavourable to high catalytic activity. When the R^1 position was substituted by a methyl group, the palladium complex **Pd4** exhibited a relatively lower activity of 11.4 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1} (entry 5 in Table 2) compared to **Pd2**, and the same trend was also found in **Pd6** with its counterpart **Pd3**. These results further proved the disadvantageous influences of electron-donating groups.

The nickel complexes bearing selected chiral ligands were also synthesized and tested for polymerization of norbornene under similar conditions. However, all the chiral nickel complexes showed much lower catalytic activity compared to their corresponding palladium complexes (entries 8–11 in Table 2), but soluble polymers were obtained and characterized by HT-GPC. The complex **Ni1** exhibited an activity of 1.5 × 10^5 g of PNB (mol of Ni)$^{-1}$ h^{-1} with a molecular weight M_n 0.82 × 10^5 g mol^{-1} (entry 8 in Table 2), while the corresponding palladium complex **Pd2** possessed nearly 20 times higher catalytic activity. When **Ni3**, the R^1 = methyl counterpart of **Ni1**, was used as a catalytic precursor, only 9.2% norbornene was finally converted to polymer after 270 minutes, that was 0.14 × 10^5 g of PNB (mol of Ni)$^{-1}$ h^{-1} in activity (entry 10 in Table 2). The influence of steric hindrance and electronic effect were also undoubtedly important in nickel-catalysed norbornene polymerization.

Direct copolymerization of olefin with a special functionalized monomer represented a simple but challenging approach to improve the properties of the original polyolefin. Based on the **Pd2**/MAO catalytic system, we turned our focus on preparing copolymers of norbornene possessing valuable functional groups.[21] Unfortunately, when polar monomers 2-acetyl-5-norbornene (ANB) and 5-norbornene-2-methanol (NBM) were used, no copolymers could be isolated. The copolymerization of norbornene with an alkenyl monomer, such as dicyclopentadiene (DCPD) or 5-vinyl-2-norbornene (VNB) have been conducted with low catalytic activity. When the ratio of VNB or DCPD to NB was 1 : 10, the activities of **Pd2** were 0.26 and 0.19 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}, respectively (Table S1†). However, the incorporation of comonomers in the obtained copolymers were rather low (*ca.* 1%). Increasing the ratio of VNB/NB to 1 : 5, the catalytic activity of **Pd2** dropped to 0.11 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}, and the incorporation of VNB was around 11.6% (see Fig. S38†) in the copolymer (M_n 2.28 × 10^4 g mol^{-1}, M_w/M_n 1.89). Further increasing the feed of VNB/NB to 1 : 1 gave only trace copolymer.

Conclusions

A series of new diarylamido-based unsymmetrical [PNN^{ox}] pincer ligands were synthesized incorporating various substituents to adjust the steric and electronic properties. The corresponding nickel and palladium complexes could be obtained easily in high yield by the reaction of (COD)$PdCl_2$ or anhydrous $NiCl_2$ with the unsymmetrical [PNN^{ox}] pincer ligands in the presence of NEt_3 at high temperature. Upon activation with MAO, the palladium complexes served as promising catalysts for vinyl-type polymerization of norbornene with an activity up to 40.3 × 10^5 g of PNB (mol of Pd)$^{-1}$ h^{-1}, while the corresponding chiral nickel complexes exhibited relatively lower activities. It has been demonstrated that the steric hindrance and electronic effect of the ligands have a significant influence on the complexes and the consequent catalytic properties. The **Pd2**/MAO system could also promote the copolymerization of alkenyl NB derivatives (DCPD and VNB) with norbornene to give copolymers with low comonomer incorporation. The study of these unsymmetrical [PNN^{ox}] pincer ligand coordinated complexes with different metal centres and their application to olefin polymerization is currently in progress.

Experimental

All the operations were carried out under a pure nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium-benzophenone. Dichloromethane was distilled from calcium hydride. Commercial reagents, namely ^{n}BuLi, methylaluminoxane (MAO), 2-fluorobenzoic acid, (*S*)-2-amino-3-methylbutan-1-ol, PPh_3, benzoxazole, and 2-fluorobenzaldehyde were purchased from TCI and used without further purification. The (COD)$PdCl_2$ complexes were synthesized according to the literature. Other commercially available reagents were purchased and used without purification. ^{1}H (400 MHz) and ^{13}C NMR (101 MHz) measurements were obtained on a JNM-ECZ400S/L 400 MR spectrometer in $CDCl_3$ solution (25 °C) or in *o*-dichlorobenzene-d_4 (120 °C). The FT-IR spectra were recorded on a NICOLET iS50 FT-IR spectrometer in the range of 4000–400 cm^{-1} by using KBr pellets. The molecular weight and molecular weight distribution of the polymers were measured by means of gel-permeation chromatography (GPC) on a PL-GPC 220 type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C.

Synthesis of the ligands

To a solution of (*S*)-2-amino-3-methylbutan-1-ol (2.67 g, 30 mmol) in acetonitrile–pyridine mixture containing 2-fluorobenzoic acid (4.20 g, 30 mmol) was successively added perchloromethane (8.7 mL, 90 mmol) and triethylamine (12.5 mL, 90 mmol) at room temperature. After stirring for 30 min, the PPh_3 dissolved in acetonitrile–pyridine mixture was added to the reaction dropwise. The reaction mixture was stirred at room temperature for at least 24 h. The solvent was evaporated and extracted with ether, after being filtered and washed with saturated copper sulfate (2 × 100 mL) and saturated salt water (2 × 100 mL), a yellow ether solution was obtained. The ether solution was dried over anhydrous Na_2SO_4 and evaporated to yield a yellow oil. The residue was purified by passing through a silica gel column with *n*-hexane/EtOAc (10 : 1) as eluent to give the corresponding **M**.

A solution of ^{n}BuLi (6.87 mL, 11 mmol, 1.6 M in hexane) was added dropwise over 10 min to a solution of 2-(diphenylphosphino)benzenamine (2.77 g, 10 mmol) in 10 mL dry THF at −78 °C. After stirring for 4 h at room temperature, the lithium solution was transferred to the solution of **M** (12 mmol) in dry THF at −78 °C. The final reacted system was slowly warmed to room temperature and then stirred for 48 h at 70 °C. The solvent was removed in vacuum and a large quantity of deionized water was added. The aqueous phases were extracted with EtOAc (4 × 100 mL), and the organic phases were dried over anhydrous Na_2SO_4. The residue was purified by passing through a silica gel column with hexane/EtOAc as eluent to give the desired **L1** as a yellow oil (1.86 g, 40%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.50 (s, 1H, Ph–N*H*–), 7.73–6.70 (m, 18H, Ph–*H*), 4.23 (m, 1H, –N–C*H*–), 3.98 (m, 2H, –O–CH_2–), 1.61 (m, 1H, –C*H*–CH_3), 0.93–0.82 (dd, 6H, –CH–CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.2, 146.4, 145.3, 145.1, 137.3, 137.2, 137.1, 137.0, 134.4, 134.1, 133.9, 132.8, 132.7, 131.6, 129.7, 129.6, 128.7, 128.6, 128.5, 124.4, 124.3, 116.9, 113.7, 110.7, 72.6, 68.2, 32.6, 19.1, 18.0. Anal. Calc. for $C_{30}H_{29}N_2OP$: C 77.57, N 6.03, H 6.29; Found: C 77.71, N 6.92, H 5.41.

L2 White solids (3.03 g, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.36 (s, 1H, Ph–N*H*–), 7.72–6.72 (m, 23H, Ph–*H*), 4.25 (dd, 1H, –N–C*H*–), 4.10 (m, 1H, –O–CH_2–), 3.95(dd, 1H, –O–CH_2–), 2.75 (m, 1H, Ph–CH_2–), 2.39 (m, 1H, Ph–CH_2–). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.8, 146.4, 145.1, 144.9, 138.1, 137.4, 137.3, 137.2, 137.1, 134.4, 134.3, 134.2, 134.1, 134.0, 131.9, 129.8, 129.7, 129.4, 128.8, 128.7, 128.6, 126.5, 124.6, 124.5, 124.4, 117.1, 113.9, 110.6, 69.8, 67.6, 41.4. Anal. Calc. for $C_{34}H_{29}N_2OP$: C 79.67, N 5.47, H 5.70; Found: C 79.11, N 5.41, H 5.77.

L3 White solids (2.59 g, 52%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.53 (s, 1H, Ph–N*H*–), 7.95–6.83 (m, 23H, Ph–*H*), 5.21 (m, 1H, –N–C*H*–), 4.65 (dd, 1H, –O–CH_2–), 4.12 (m, 1H, –O–CH_2–). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 165.0, 146.7, 145.0, 144.8, 142.9, 137.2, 137.1, 136.9, 136.8, 134.5, 134.4, 134.2, 134.0, 133.8, 133.0, 132.9, 132.2, 130.2, 129.7, 128.8, 128.7, 128.6, 128.5, 128.4, 127.4, 126.8, 124.6, 117.2, 114.1, 110.5, 73.3, 69.9. Anal. Calc. for $C_{33}H_{27}N_2OP$: C 79.50, N 5.62, H 5.46; Found: C 79.08, N 5.41, H 5.64.

L4 White solids (3.13 g, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.95 (s, 1H, Ph–N*H*–), 7.46–6.62 (m, 21H, Ph–*H*), 4.19 (m, 1H, –N–C*H*–), 4.04 (m, 1H, –O–CH_2–), 3.89 (m, 1H, –O–CH_2–), 2.66 (d, 1H, Ph–CH_2–), 2.32 (m, 1H, Ph–CH_2–), 2.21 (s, 3H, CH_3–Ph), 2.19 (s, 3H, CH_3–Ph). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.8, 144.6, 142.9, 142.6, 138.2, 137.6, 137.5, 137.4, 137.3, 134.5, 134.2, 134.1, 134.0, 133.9, 133.7, 132.8, 132.2, 132.1, 130.5, 129.7, 129.4, 128.7, 128.6, 128.5, 126.4, 125.8, 124.5, 124.4, 114.0, 110.2, 69.8, 67.6, 41.4, 21.2, 20.5. Anal. Calc. for $C_{36}H_{33}N_2OP$: C 79.98, N 5.18, H 6.15; Found: C 79.48, N 5.06, H 6.25.

L5 Yellow oil (2.79 g, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.93 (s, 1H, Ph–N*H*–), 7.56–6.81 (m, 21H, Ph–*H*), 5.05 (s, 1H, –N–C*H*–), 4.54 (s, 1H, –O–CH_2–), 3.98 (d, 1H, –O–CH_2–), 2.23 (s, 3H, CH_3–Ph), 2.17 (s, 3H, CH_3–Ph). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 164.9, 144.9, 142.9, 137.4, 137.3, 137.0, 136.9, 134.7, 134.5, 134.3, 134.1, 133.9, 133.1, 130.5, 129.9, 129.0, 128.8, 128.6, 128.5, 128.4, 128.1, 127.3, 126.0, 125.8, 124.7, 124.6, 114.2, 110.1, 73.2, 69.9, 21.3, 20.6. Anal. Calc. for $C_{35}H_{33}N_2OP$: C 79.83, N 5.32, H 5.93; Found: C 79.80, N 5.18, H 6.05.

L6 White solids (2.16 g, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.43 (s, 1H, Ph–N*H*–), 7.72–6.70 (m, 18H, Ph–*H*), 3.92 (m, 2H, –O–CH_2–), 1.14–0.99 (m, 6H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 161.7, 146.2, 145.4, 145.1, 137.4, 137.3, 134.6, 134.0, 133.9, 133.8, 132.0, 131.9, 131.6, 129.6, 129.5, 128.6, 128.5, 124.2, 117.0, 113.8, 110.9, 67.8, 28.3. Anal. Calc. for $C_{29}H_{27}N_2OP$: C 77.31, N 6.22, H 6.04; Found: C 77.13, N 5.93, H 6.35.

Synthesis of L7

To a solution of benzoxazole (7.14 g, 60 mmol) and 2-fluorobenzaldehyde (3.72 g, 30 mmol) in PhCl (30 mL) was added

dry DMF (3 mL) at room temperature. The crude reaction mixture was filtered under nitrogen, followed by the addition of I_2 (15.24 g, 60 mmol), and then stirred for 48 h at 130 °C. The solution was cooled to room temperature and 60 mL saturated $Na_2S_2O_3$ added. After extraction with EtOAc (4 × 100 mL) and drying over anhydrous Na_2SO_4, the solution was evaporated to yield a brown oil. The residue was purified by passing through a silica gel column with hexane/EtOAc as eluent, giving the corresponding 2-(2-fluorophenyl) benzoxazole.

The ligand **L7** was synthesized in a similar way as for the synthesis of ligand **L1** with the usage of 2-(2-fluorophenyl)benzoxazole. Pure products were obtained as white solids by column chromatography with hexane/EtOAc as eluent (1.55 g, 33%) ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.01 (s, 1H, Ph–N*H*–), 8.08–6.79 (m, 22H, Ph–*H*). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 162.7, 149.2, 145.9, 144.5, 144.3, 137.0, 136.9, 134.4, 134.2, 134.0, 133.7, 133.6, 132.2, 129.8, 128.9, 128.8, 128.7, 128.6, 125.6, 125.5, 125.1, 124.7, 124.1, 119.8, 117.7, 114.3, 110.2, 110.0. Anal. Calc. for $C_{31}H_{23}N_2OP$: C 79.14, N 5.95, H 4.93; Found: C 78.89, N 5.69, H 5.13.

Synthesis of the metal complexes

To a solution of $(COD)PdCl_2$ (57.1 mg, 0.2 mmol) or $NiCl_2$ (25.9 mg, 0.2 mmol) in dry toluene containing the ligand (0.2 mmol) was added triethylamine (0.03 mL, 0.22 mmol) at room temperature, and the mixture was stirred for 5 h at 70 °C. The reaction mixture was filtered under nitrogen and the filtrate was concentrated under reduced pressure to *ca.* 2 mL, and then dry hexane (15 mL) was added. Solvent was removed from the precipitate *via* cannula filtration, and the residue was washed with *n*-hexane. Recrystallization of the crude product from CH_2Cl_2/hexane gave the desired complex.

Pd1 Red powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.87–6.56 (m, 18H, Ph–*H*), 4.84 (s, 1H, –N–C*H*–), 4.43 (d, 2H, –O–CH_2–), 2.60 (s, 1H, –C*H*–CH_3), 1.28 (d, 3H, –CH–CH_3), 1.24 (d, 3H, –CH–CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.2, 146.4, 145.3, 145.1, 137.3, 137.2, 137.1, 137.0, 134.4, 134.1, 133.9, 133.7, 132.8, 132.7, 131.6, 129.7, 129.6, 128.8, 128.6, 128.5, 128.4, 124.4, 116.9, 113.6, 110.7, 72.6, 68.2, 32.6, 19.1, 18.0. Due to the residual solvent, we were unable to obtain satisfactory elemental analysis data.

Pd2 Red powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.92–6.56 (m, 23H, Ph–*H*), 5.16 (m, 1H, –N–C*H*–), 4.40 (m, 2H, –O–CH_2–), 3.72 (d, 1H, Ph–*H*), 2.85 (d, 1H, Ph–*H*). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.9, 163.7, 163.5, 153.6, 137.1, 134.2, 134.1, 133.9, 132.9, 132.8, 132.5, 132.1, 131.5, 131.3, 131.1, 129.8, 129.2, 129.1, 129.0, 128.8, 128.6, 128.3, 126.8, 121.2, 121.1, 120.0, 119.9, 119.8, 117.4, 72.5, 64.3, 42.0.

Pd3 Red powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.85–6.59 (m, 23H, Ph–*H*), 6.01 (m, 1H, –N–C*H*–), 4.87 (m, 1H, –O–CH_2–), 4.58 (dd, 1H, –O–CH_2–). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 164.0, 163.7, 163.5, 154.1, 142.0, 134.3, 134.2, 133.8, 132.8, 132.7, 131.9, 131.5, 131.4, 131.2, 129.9, 129.1, 129.0, 128.9, 128.6, 128.5, 127.9, 127.3, 123.0, 122.4, 121.3, 121.1, 119.9, 119.8, 119.7, 117.3, 114.7, 76.4, 66.2.

Pd4 Red powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.95–6.79 (m, 21H, Ph–*H*), 5.19 (s, 1H, –N–C*H*–), 4.39 (d, 2H, –O–CH_2–), 3.72 (d, 1H, Ph–*H*), 2.90 (d, 1H, Ph–*H*), 2.20 (d, 3H, CH_3–Ph), 2.17 (d, 3H, CH_3–Ph). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.5, 163.4, 162.0, 161.8, 151.8, 137.2, 134.3, 134.1, 133.7, 133.3, 133.0, 132.9, 131.5, 131.3, 130.6, 130.3, 129.9, 129.1, 129.0, 128.9, 128.7, 128.6, 128.3, 126.8, 126.2, 122.4, 121.9, 121.0, 120.8, 119.6, 114.4, 72.5, 64.3, 42.0, 20.4, 20.3.

Pd5 Red powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.85–6.72 (m, 21H, Ph–*H*), 6.03 (dd, 1H, –N–C*H*–), 4.86 (t, 1H, –O–CH_2–), 4.57 (dd, 1H, –O–CH_2–), 2.20 (m, 3H, CH_3–Ph), 2.16 (m, 3H, CH_3–Ph). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.9, 163.8, 161.8, 161.6, 152.2, 142.1, 134.3, 134.2, 133.9, 133.2, 133.1, 132.8, 132.7, 131.4, 131.3, 131.1, 131.0, 130.7, 130.3, 129.8, 129.1, 128.9, 128.6, 128.5, 128.4, 127.8, 127.3, 126.1, 121.0, 120.8, 119.6, 114.2, 66.1, 20.4, 20.3.

Pd6 Red powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.90–6.61 (m, 18H, Ph–*H*), 4.32 (d, 1H, –O–CH_2–), 4.13 (d, 1H, –O–CH_2–), 1.80 (d, 3H, –C–CH_3), 1.70 (d, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.7, 163.5, 153.3, 134.3, 134.2, 133.7, 132.9, 132.8, 132.1, 131.5, 131.4, 131.3, 131.2, 130.1, 129.6, 129.1, 128.9, 128.6, 128.5, 123.2, 122.6, 121.4, 121.2, 119.8, 119.7, 117.5, 117.4, 29.0, 28.1.

Pd7 Red powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.79–6.69 (m, 22H, Ph–*H*). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.4, 153.5, 134.2, 134.1, 133.7, 133.0, 132.9, 132.6, 132.4, 131.8, 131.7, 131.6, 131.5, 130.3, 129.2, 129.1, 128.8, 128.6, 125.5, 125.2, 124.5, 122.0, 121.8, 121.2, 120.5, 120.4, 120.2, 118.2, 115.9, 110.3.

Ni1 Green powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.91–6.53 (m, 23H, Ph–*H*), 4.86 (m, 1H, –N–C*H*–), 4.30 (m, 2H, –O–CH_2–), 3.83 (m, 1H, Ph–*H*), 3.05 (dd, 1H, Ph–*H*). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.8, 146.3, 145.0, 144.8, 138.1, 137.3, 137.2, 137.1, 137.0, 134.3, 134.2, 134.1, 134.0, 133.9, 132.4, 132.3, 131.8, 131.1, 131.0, 129.8, 129.7, 129.4, 128.7, 128.6, 128.5, 126.4, 124.4, 117.0, 113.9, 110.6, 69.8, 67.6, 41.3.

Ni2 Green powder.^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.76–6.47 (m, 23H, Ph–*H*), 5.73 (dd, 1H, –N–C*H*–), 4.82 (dd, 1H, –O–CH_2–), 4.47 (dd, 1H, –O–CH_2–). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 164.5, 144.7, 145.5, 142.6, 134.9, 134.8, 133.2, 132.0, 131.9, 131.8, 131.7, 131.6, 131.5, 131.4, 131.3, 131.2, 129.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.4, 126.7, 124.2, 124.0, 117.6, 114.0, 110.9, 73.4, 69.8.

Ni3 Green powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.94–6.72 (m, 21H, Ph–*H*), 4.88 (dd, 1H, –N–C*H*–), 4.33 (m, 2H, –O–CH_2–), 3.86 (dd, 1H, Ph–*H*), 3.08 (dd, 1H, Ph–*H*), 2.16 (m, 6H, CH_3–Ph). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 162.7, 161.2, 160.9, 151.6, 137.3, 134.1, 134.0, 133.1, 132.9, 132.5, 132.4, 130.9, 129.9, 129.5, 129.4, 129.2, 129.1, 129.0, 128.8, 128.6, 128.5, 128.3, 126.8, 125.5, 125.4, 124.6, 124.1, 120.8, 120.7, 120.6, 114.2, 71.9, 62.7, 42.3, 20.4, 20.3.

Ni4 Green powder. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.76–6.65 (m, 21H, Ph–*H*), 5.73 (dd, 1H, –N–C*H*–), 4.80 (t, 1H, –O–CH_2–), 4.45 (dd, 1H, –O–CH_2–), 2.20 (m, 3H, CH_3–Ph), 2.11 (m, 3H, CH_3–Ph). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm): δ 163.1,

160.9, 160.7, 151.8, 142.9, 134.2, 134.1, 133.2, 132.7, 132.6, 132.5, 132.4, 132.3, 130.7, 130.6, 129.9, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.4, 128.3, 128.2, 127.8, 127.5, 125.6, 120.8, 120.5, 120.3, 113.9, 75.8, 65.0, 20.3.

X-ray crystallography

Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2/*n*-hexane solutions. The intensity data of the single crystals were collected on the CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All data were collected at room temperature using the ω scan technique. These structures were solved by direct methods using Fourier techniques and refined on F^2 by a full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. Crystallographic data are summarized in Table S2.†

Crystallographic data (excluding structure factors) for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1854348 (**Pd1**), 1854347 (**Pd2**), 1854349 (**Pd6**) and 1854346 (**Pd7**).†

Polymerization of norbornene

In a typical synthesis, 1.5 μmol of complex and 1.0 g of norbornene in toluene (1.5 mL) were placed in a 25 mL special polymerization bottle with a strong stirrer under a nitrogen atmosphere. After the mixture was kept at room temperature for 10 min, MAO (10 wt% in toluene) was charged into the polymerization system *via* a syringe and the reaction was initiated. Several minutes later, acidic ethanol ($V_{ethanol}/V_{concd.\ HCl}$ = 20/1) was added to terminate the reaction. The PNB was isolated by filtration, washed with ethanol, and dried at 80 °C for 24 h under vacuum. For all polymerization procedures, the total reaction volume was 10.0 mL, which can be achieved by varying the amount of toluene when necessary.

Copolymerization of norbornene with 5-vinyl-2-norbornene

Copolymerization was carried out under a nitrogen atmosphere in toluene with a mechanical stirrer. The norbornene and 5-vinyl-2-norbornene in 1.0 mL of toluene, 1.5 μmol of complex in 0.5 mL of toluene were placed in the bottle, and another 1.5 mL of fresh toluene was added to adjust the total volume to 10 mL. After the mixture was stirred at room temperature for 10 min, 7.0 mL of MAO was charged into the polymerization system *via* syringe and the reaction was initiated. Several minutes later, acidic ethanol ($V_{ethanol}/V_{concd.HCl}$ = 20/1) was added to terminate the reaction. The copolymer was isolated by filtration, washed with ethanol, and dried at 80 °C for 12 h under vacuum.

The incorporation of 5-vinyl-2-norbornene were calculated from the 1H NMR spectrum according to the following formula.

$$\text{Incorp. } (\%) = \{(10I_{H1} + 10I_{H2})/(I_{H1} + I_{H2} + 3I_{H3})\} \times 100\%$$

in which I_{H1} is the integration of the signals at 5.81–5.60 ppm (vinyl proton of the norbornene derivative unit), I_{H2} is the integration of the signals at 4.87–4.65 ppm (vinyl proton of the norbornene derivative unit), and I_{H3} is the integration of the signals at 2.13–0.67 ppm (proton of the norbornene unit) in the ^{1}H NMR spectrum.

Conflicts of interest

There are no conflicts to declare.

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