

Novel highly active binuclear neutral nickel and palladium complexes as precatalysts for norbornene polymerization

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Abstract

A series of binuclear neutral nickel and palladium complexes $[(XC_6H_2CH=NC_6H_3-iPr_2)MRL]_2$ **4b–f** (X = NO₂, M = Ni, R = Ph, L = PPh₃, **4b**; X = H, M = Pd, R = Me, L = PPh₃, **4c**; X = H, M = Pd, R = Me, L = Py, **4d**; X = NO₂, M = Pd, R = Me, L = PPh₃, **4e**; X = NO₂, M = Pd, R = Me, L = Py, **4f**) and $[(C_{10}H_7CH=NC_6H_3-iPr_2)MRL]_2$ **8a–c** (M = Ni, R = Ph, L = PPh₃, **8a**; M = Pd, R = Me, L = PPh₃, **8b**; M = Pd, R = Me, L = Py, **8c**) have been synthesized and characterized. The structures of complexes **4e** and **8b** have also been confirmed by X-ray crystallographic analysis. With modified methylaluminoxane (MMAO) as cocatalysts, these complexes and complex $[(C_6H_3CH=NC_6H_3-iPr_2)NiPh(PPh_3)_2]$ **4a** are capable of catalyzing the addition polymerization of norbornene (NBE) with the high activity up to 2.3×10^8 g PNBE/(mol_M h). The structure of complexes affects considerably catalytic activity towards norbornene polymerization. The polymers obtained with nickel complexes are soluble, while those obtained with palladium complexes are insoluble. Palladium complexes **4c**, **4e** and **8b** bearing PPh₃ ligands exhibit much higher activities than the corresponding complexes **4d**, **4f** and **8c** bearing pyridine ligands under the same conditions.

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1. Introduction

For the past several years, interest in neutral late transition metal complexes as olefin polymerization catalysts has been on the rise because neutral complexes are less electrophilic than the corresponding cationic ones [1–8]. Early in the research, the modified SHOP catalysts were developed to convert ethylene to high molecular weight polymers [9]. Recently, Grubbs and co-workers found that neutral salicylaldimine-based nickel(II) complexes with bulky *O-ortho* substituents are highly active single-component catalysts towards ethylene polymerization [10–12], which greatly stimulated the researchers in this area. Subsequently, some neutral nickel(II) complexes with novel ligands were developed to catalyze ethylene polymerization [13–19]. In addition, the neutral palladium(II) catalysts have also been

reported by Novak and co-workers [20], Sen and co-workers [21] and our group [22].

During the past few years, we have found that the neutral nickel complexes, based on pyrrole-imine and salicylaldimine ligands, exhibit very high activities for vinylic norbornene polymerization in the presence of modified methylaluminoxane (MMAO) [23,24]. Recently, several mononuclear nickel(II) complexes [25–29] and binuclear nickel and palladium complexes [30–32] were utilized to catalyze norbornene polymerization by means of activation with different co-catalysts, which has greatly deepened this research field. More recently, we have developed a novel binuclear Ni(II) complex based on the bis(salicylaldimine) ligand, which displays higher activity towards ethylene polymerization and produces the polyethylenes with broader molecular weight distribution than mononuclear salicylaldimine–Ni(II) complexes [33]. This urges us to check if there are analogous trends when the binuclear and mononuclear salicylaldimine-based neutral nickel or palladium complexes are used to catalyze norbornene polymerization.

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Here, we report the syntheses and characterizations of a series of binuclear neutral nickel(II) and palladium(II) complexes **4b–f** and **8a–c** based on bis(salicylaldehyde)-type ligands. For these complexes, each salicylaldehyde derivative unit serves as a bulky group at C-3 position of the other unit. The behavior of these complexes towards norbornene polymerization is investigated.

2. Results and discussion

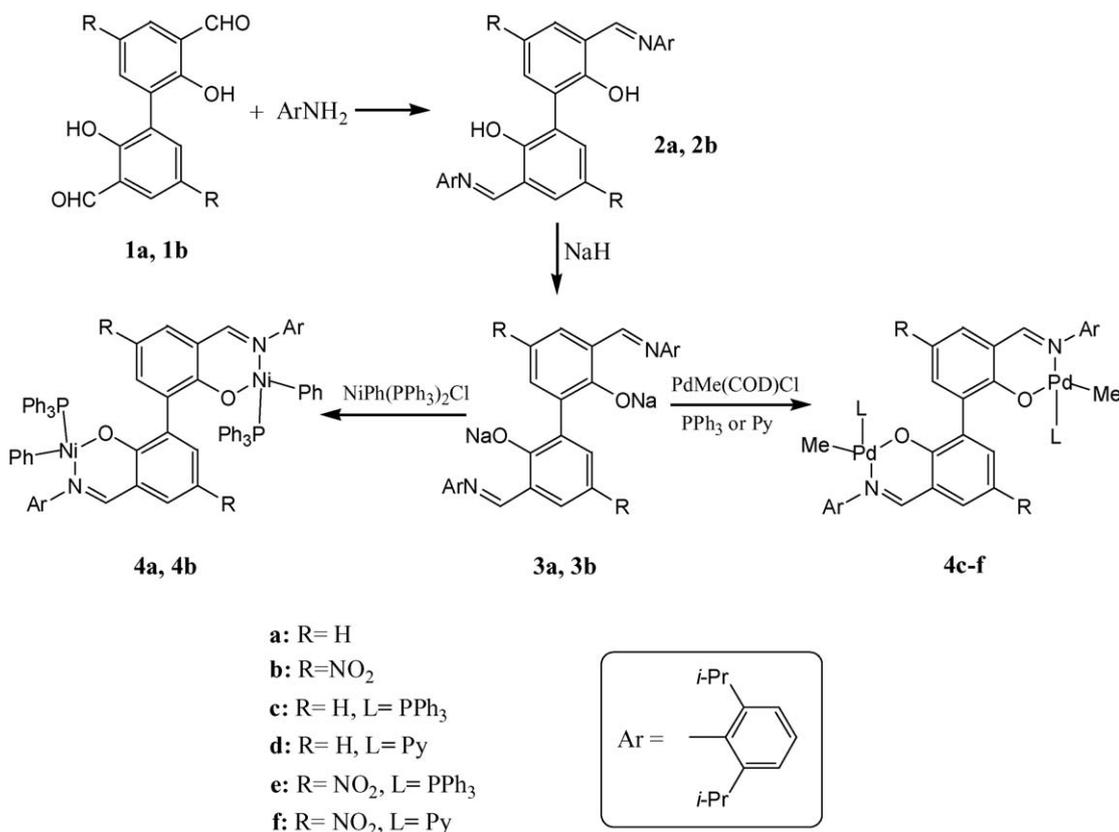
2.1. Synthesis and structure of complexes

The synthetic routes for binuclear complexes **4b–f** and **8a–c** are shown in Schemes 1 and 2, respectively. The free ligands **2a**, **2b** and **6** were synthesized via the condensation reaction of excess 2,6-diisopropylaniline and the corresponding compounds **1a**, **1b** and **5**, respectively, in good yields (**2a**, 73%; **2b**, 92%; **6**, 99%). The deprotonation of the ligands **2a**, **2b** and **6** readily proceeded with excess sodium hydride in anhydrous THF at room temperature. The reaction of isolated sodium salts **3a**, **3b** and **7** with two equivalent of *trans*-NiCl(Ph)(PPh₃)₂, (COD)PdMeCl/PPh₃ or (COD)PdMeCl/pyridine for 14 h afforded corresponding binuclear complexes **4b–f** and **8a–c**, respectively.

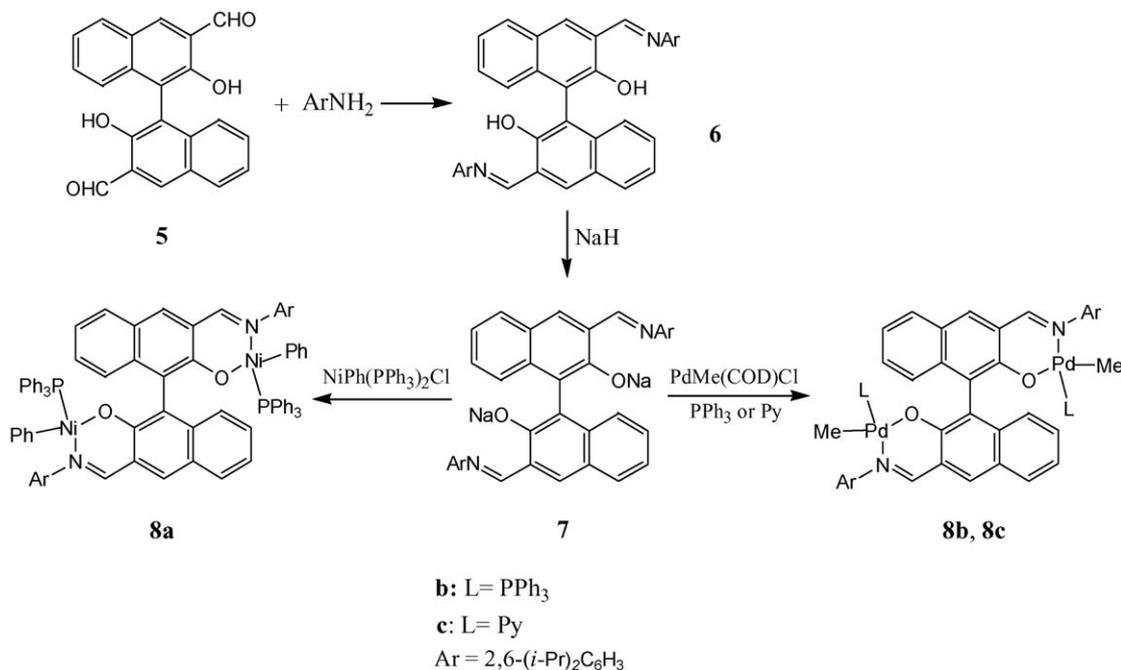
In the syntheses of palladium complexes, the sequence of addition of reactants is crucial. Addition of a solution of sodium salt **3b** in benzene to the solution containing (COD)PdMeCl and

pyridine (Py) gave a yellow complex Py₂PdMeCl (confirmed by X-ray analysis and ¹H NMR) without the bis(salicylaldehyde)-type ligand, instead of **4d**. Therefore, we believe that it is critical that the sodium salts **3a** and **3b** should be added to (COD)PdMeCl and be stirred for a while, followed by the addition of pyridine or PPh₃, in view of the strong binding strength of pyridine or PPh₃ with palladium atom. In addition, for the syntheses of **4e** and **4f**, CH₂Cl₂ was used as solvent in place of benzene due to the insolubility of sodium salt **3b** in benzene.

The molecular structures of complexes **4e** and **8b** were confirmed by single-crystal X-ray structure analyses. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a concentrated solution of **4e** in CH₂Cl₂ and **8b** in benzene, respectively. The crystallographic data together with the collection and refinement parameters are summarized in Table 1, and their ORTEP diagrams are shown in Figs. 1 and 2. The selected bond lengths and angles for **4e** and **8b** are given in Tables 2 and 3. In the solid state, they adopt geometries best described as square planar about each palladium center, having slight distortions from idealized geometry. The deviations of two Pd atoms from the plane of their ligands are approximately 0.016 Å (**4e**-Pd1) and 0.011 Å (**4e**-Pd2), 0.053 Å (**8b**-Pd1) and 0.025 Å (**8b**-Pd2), respectively. The bulky 2,6-diisopropylbenzimidine occupies the position *trans* to the triphenylphosphine ligand with a nearly linear P–Pd–N angle. The CH₃ group attached to the Pd atom lies *trans* to the O atom



Scheme 1.



Scheme 2.

Table 1
Crystal data and structure refinement for complexes **4e** and **8b**

	4e · CH ₂ Cl ₂	8b · 4.5C ₆ H ₆
Empirical formula	C ₇₇ H ₇₈ Cl ₂ N ₄ O ₆ P ₂ Pd ₂	C ₁₁₁ H ₁₀₉ N ₂ O ₂ P ₂ Pd ₂
fw	1501.07	1777.74
Cryst syst	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	22.4715(13)	14.4910(9)
<i>b</i> (Å)	104823(6)	15.1753(9)
<i>c</i> (Å)	32.8045(19)	22.5290(14)
<i>V</i> (Å ³)	7496.0(7)	4576.2(5)
α (°)	90	73.4640(10)
β (°)	104.0520(10)	74.6710(10)
γ (°)	90	83.4240(10)
<i>Z</i>	4	2
<i>D</i> _{calc} (Mg/m ³)	1.330	1.290
Abs coeff. (mm ⁻¹)	0.646	0.480
<i>F</i> (000)	3088	1854
Crystal size (mm)	0.50 × 0.15 × 0.08	0.43 × 0.24 × 0.14
θ range (°)	1.92 to 26.03	1.46 to 26.04
No. of indep rflns	14633 (<i>R</i> _{int} = 0.0316)	17544 (<i>R</i> _{int} = 0.0188)
Abs corr	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmn	0.9477 and 0.7304	0.9367 and 0.8205
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0565, <i>wR</i> ₂ = 0.1503	<i>R</i> ₁ = 0.0540, <i>wR</i> ₂ = 0.1304
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0673, <i>wR</i> ₂ = 0.1600	<i>R</i> ₁ = 0.0613, <i>wR</i> ₂ = 0.1348
Largest diff. peak and hole	3.557 and -0.924e Å ⁻³	2.735 and -1.268e Å ⁻³
Type of diffractometer	Bruker SMART	Bruker SMART
Monochromator	Graphite	Graphite

Table 2
Selected bond distances (Å) and angles (°) for **4e**

Pd(1)–C(1)	2.041(4)	P(1)–C(20)	1.823(4)
Pd(1)–O(1)	2.080(3)	P(1)–C(26)	1.824(5)
Pd(1)–N(1)	2.088(3)	P(1)–C(14)	1.829(4)
Pd(1)–P(1)	2.2328(11)	N(1)–C(32)	1.291(5)
Pd(2)–C(76)	2.046(4)	N(1)–C(2)	1.455(5)
Pd(2)–O(4)	2.086(3)	N(2)–O(2)	1.229(5)
Pd(2)–N(3)	2.103(3)	N(2)–C(37)	1.443(5)
Pd(2)–P(2)	2.2302(11)		
C(1)–Pd(1)–O(1)	176.38(19)	O(4)–Pd(2)–P(2)	94.10(8)
C(1)–Pd(1)–N(1)	91.18(16)	N(3)–Pd(2)–P(2)	173.89(10)
O(1)–Pd(1)–N(1)	89.62(12)	C(20)–P(1)–C(26)	107.8(2)
C(1)–Pd(1)–P(1)	85.36(13)	C(20)–P(1)–Pd(1)	112.80(15)
O(1)–Pd(1)–P(1)	94.16(8)	C(32)–N(1)–C(2)	113.8(3)
N(1)–Pd(1)–P(1)	173.75(11)	C(32)–N(1)–Pd(1)	122.3(3)
C(76)–Pd(2)–O(4)	172.77(17)	C(2)–N(1)–Pd(1)	123.3(2)
C(76)–Pd(2)–N(3)	92.85(15)	O(2)–N(2)–O(3)	122.2(4)
O(4)–Pd(2)–N(3)	88.40(12)	O(2)–N(2)–C(37)	119.5(3)
C(76)–Pd(2)–P(2)	85.37(13)		

Table 3
Selected bond distances (Å) and angles (°) for **8b**

Pd(1)–C(24)	2.041(4)	Pd(2)–P(2)	2.2515(10)
Pd(1)–O(1)	2.091(3)	P(1)–C(37)	1.815(4)
Pd(1)–N(1)	2.094(3)	P(1)–C(25)	1.825(4)
Pd(1)–P(1)	2.2314(10)	P(1)–C(31)	1.828(4)
Pd(2)–C(66)	2.032(4)	O(1)–C(3)	1.308(4)
Pd(2)–N(2)	2.094(3)	N(1)–C(1)	1.285(5)
Pd(2)–O(2)	2.094(3)	N(1)–C(12)	1.450(4)
C(24)–Pd(1)–O(1)	174.70(16)	C(66)–Pd(2)–O(2)	173.7(2)
C(24)–Pd(1)–N(1)	89.86(14)	C(37)–P(1)–C(25)	108.67(19)
O(1)–Pd(1)–N(1)	88.81(11)	C(37)–P(1)–Pd(1)	110.09(13)
C(24)–Pd(1)–P(1)	86.50(12)	C(3)–O(1)–Pd(1)	122.3(2)
O(1)–Pd(1)–P(1)	94.76(8)	C(1)–N(1)–C(12)	114.6(3)
N(1)–Pd(1)–P(1)	176.31(9)	C(1)–N(1)–Pd(1)	121.6(2)
C(66)–Pd(2)–N(2)	89.57(15)	C(12)–N(1)–Pd(1)	123.9(2)

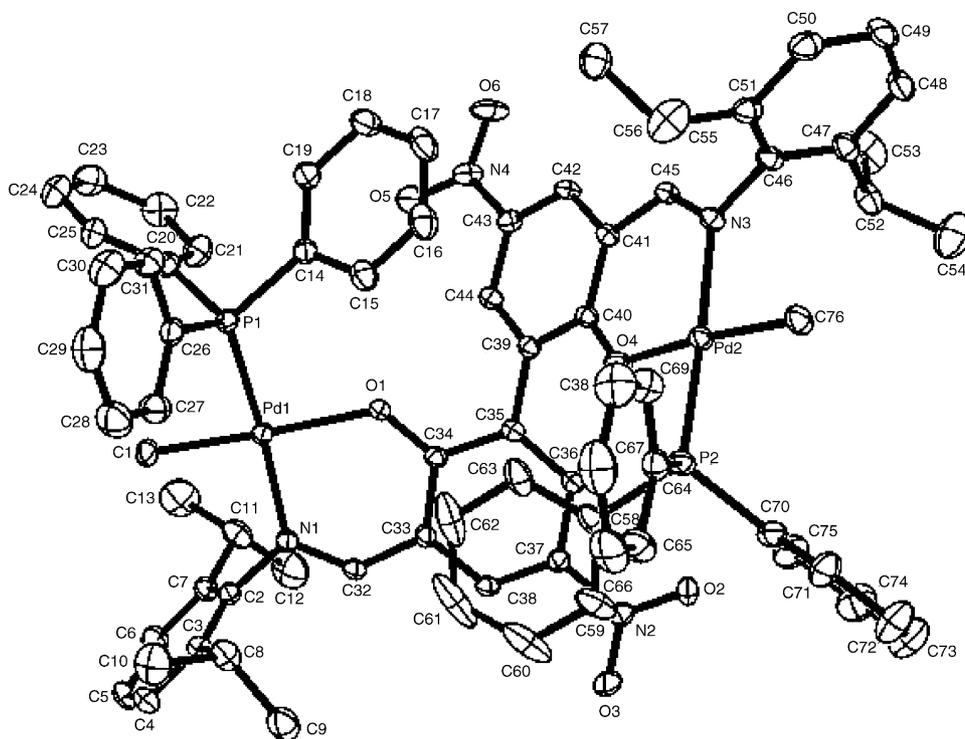


Fig. 1. ORTEP view of complex **4e** (A CH_2Cl_2 molecules of crystallization are omitted).

with an O–Pd–C angle higher than 172.5° . For **4e**, two planes defined by the atoms of the salicylideneiminato fragment form an approximately perpendicular angle (101.2°). Comparatively, the corresponding angle is only 40.2° for **8b**.

2.2. Polymerization of norbornene

Preliminary experiments have indicated that these binuclear neutral (salicylaldehyde)Ni(II) and (salicylaldehyde)Pd(II)

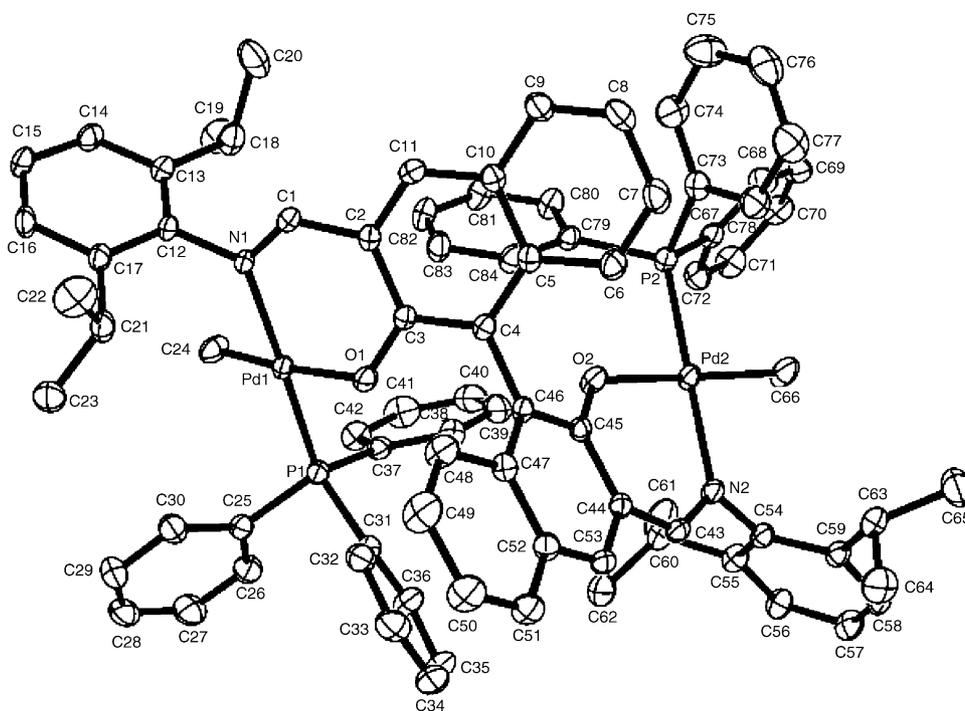


Fig. 2. ORTEP view of complex **8b** (4.5 benzene solvent molecules of crystallization are omitted).

Table 4
Norbornene polymerization results catalyzed by **4a–f** and **8a–c**/MMAO

Entry	Catalyst	Norbornene feeds (g)	Time (min)	Temperature (°C)	Al:metal (mol ratio)	Polymer (g)	Yield (%)	10^{-7} Activity ^a	$10^{-6} M_w^b$	PDI ^b	T_g (°C) ^c
1	4a	3.31	5	20	2000	3.12	94	7.49	1.84	3.72	324
2	4b	3.31	5	20	2000	3.22	97	7.73	1.60	3.36	314
3	8a	3.31	5	20	2000	3.05	92	7.31	1.76	3.51	329
4	4c	4.14	2	50	3000	3.78	91	22.7	n.d.	n.d.	325
5	4c	3.31	5	20	2000	1.33	40	3.19	n.d.	n.d.	330
6	4c	3.31	5	40	2000	3.04	92	7.29	n.d.	n.d.	330
7	4d	4.14	2	50	3000	0.42	10	2.52	n.d.	n.d.	320
8	4e	4.14	2	50	3000	3.64	88	21.8	n.d.	n.d.	319
9	4f	4.14	2	50	3000	0.47	11	2.82	n.d.	n.d.	321
10	8b	4.14	2	50	3000	3.44	83	20.6	n.d.	n.d.	318
11	8c	4.14	2	50	3000	0.14	3.4	0.84	n.d.	n.d.	325

All the polymerizations run using 0.25 μ mol catalyst with $V_{\text{total}} = 30$ ml.

^a In units of g PNBE/(mol_M h).

^b Determined by GPC and n.d. means the sample was not determined.

^c T_g is determined by DSC.

complexes are not able to catalyze norbornene polymerization without cocatalysts. As we all know, MMAO alone is also inactive for norbornene polymerization [23,24]. Interestingly, in combination with MMAO, these neutral (salicylaldimine)M(II) (M=Ni, Pd) complexes **4a–f** and **8a–c** exhibit extremely high catalytic activity for norbornene polymerization under moderate conditions. Especially for **4c** and **4e**, norbornene can be rapidly converted into white polynorbornene (PNBE) powder with higher than 88% yield within 2 min. The typical results are summarized in Table 4. The bis(salicylaldimine)Ni(II)/MMAO systems display higher activities ($7.31\text{--}7.73 \times 10^7$ g PNBE/(mol_{Ni} h), Entries 1–3 in Table 4) than the mononuclear salicylaldimine–Ni-based complexes with or without substituents on the phenoxy fragment (5.11×10^7 g PNBE/(mol_{Ni} h)) [23] under similar conditions. Although there is a sharp difference in the steric structures of complexes **4a** and **8a**, the catalytic activities of the two complexes are very close. This indicates that the dimension of substituents on the phenoxy fragment have little influence on the catalytic activity towards norbornene polymerization, which is different from ethylene polymerization [10–12].

For palladium complexes, bis(salicylaldimine)-based **4c** and **4e** show high catalytic activities up to 2.3×10^8 g PE/(mol_{Pd} h) (Entries 4 and 8 in Table 4). To well understand the difference between binuclear neutral palladium complex and the corresponding mononuclear one, we synthesized salicylaldimine-based palladium complex $\{\eta^2\text{-}1\text{-}[\text{CH}=\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]\text{-}2\text{-O-C}_6\text{H}_4\}\text{-Pd}(\text{CH}_3)_2\text{PPh}_3$ and evaluated its catalytic behavior under the same conditions. This mononuclear complex displays much lower activity (6.6×10^7 g PNBE/(mol_{Pd} h)) than the corresponding binuclear complexes **4c** and **4e**. Obviously, bulky groups in the three-position of the salicylaldiminato fragment are responsible for the high catalytic activities of the binuclear palladium complexes. It is noteworthy that **4c** displays a slightly higher activity than **8b** (Entries 4 and 10 in Table 4), which seems to indicate that very bulky substituents in the three-position of the salicylaldiminato fragment are not advantageous to norbornene polymerization. A possible reason for this is that very bulky

steric hindrance restricts the insertion of cyclic norbornene to Pd center and the growth of polynorbornene chain. Additionally, the NO₂ group on the phenoxy group slightly raises the catalytic activities of the Ni complexes (Entries 1 and 2 in Table 4), which is similar to the mononuclear neutral Ni complexes catalyzing ethylene polymerization [10–12]. However, for the palladium complexes **4e** and **4f** (Entries 8 and 9 in Table 4), this effect of the NO₂ group does not appear.

Surprisingly, palladium complexes with pyridine as a neutral ligand exhibit much lower activities (Entries 7, 9 and 11 in Table 4) than those (Entries 4, 8 and 10 in Table 4) with PPh₃ as a neutral ligand. When the polymerization time was prolonged from 2 to 20 min, the PNBE yield only slightly increased for the palladium complexes with the pyridine ligand. As a matter of fact, the PPh₃ ligand has stronger binding strength with Pd than pyridine. On the basis of the need to dissociate the donor ligands to free a coordination site for monomer, it is reasonable to expect that complexes bearing the pyridine ligand have reasonably higher activity than those bearing the PPh₃ ligand. Therefore, we speculate that this difference is due to the fact that the bulky PPh₃ dissociates more easily than small pyridine under the activation with MMAO.

Up to now, the active species in MAO- or B(C₆F₅)₃-activated nickel or palladium complex for norbornene polymerization have not been clarified. Interestingly, the “naked” Pd²⁺ cations were considered highly active species of the norbornene polymerization [34]. However, in our cases, the distinct difference between binuclear neutral palladium complex and the corresponding mononuclear one in catalytic behavior suggests that the bulky groups in the three-position of the salicylaldiminato fragment substantially affect the catalytic activities of the palladium complexes, which indirectly indicates the [N,O]-chelate ligands remain bound to the palladium center upon activation. About the actual active species and the catalytic mechanism, the relevant research is underway.

To further investigate the norbornene polymerization behavior of these catalyst precursors, polymerizations were also investigated under varied reaction conditions. Although similar

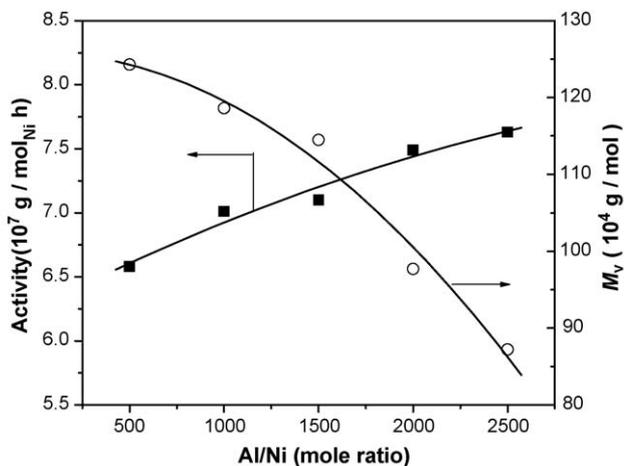


Fig. 3. Plot of activity and M_v vs. Al/Ni (molar ratio); 20 °C, 0.25 μmol **4a**, 3.31 g of norbornene feeds, $V_{\text{total}} = 30$ ml, 5 min polymerization run.

investigations were done before [35,36], for a new class of precatalysts, it is necessary to investigate the effects of reaction conditions on the polymerization behavior. Variation of the molar ratio of MMAO to precatalyst **4a**, which is expressed here as the Al/Ni ratio, showed effects on the catalytic activity and polymer molecular weights. As shown in Fig. 3, the catalytic activity slightly increases from 6.58×10^7 to 7.63×10^7 g PNBE/(mol_{Ni} h) when the mole ratio of Al/Ni increases from 500/1 to 2500/1. In contrast, the viscosity-average molecular weight (\bar{M}_v) of the polymers decreases sharply with the increase in the Al/Ni ratio due to the chain transfer to MMAO. As for palladium precatalyst **4c**, the catalytic activity slowly increases with the increase in the molar ratio of MMAO to **4c** (Al/Pd ratio) and reaches the highest value at Al/Pd ratio = 2500, and then turns to decrease (Fig. 4(a)).

The reaction temperature also affects the catalytic activity of precatalyst **4a** and molecular weights of the polynorbornenes.

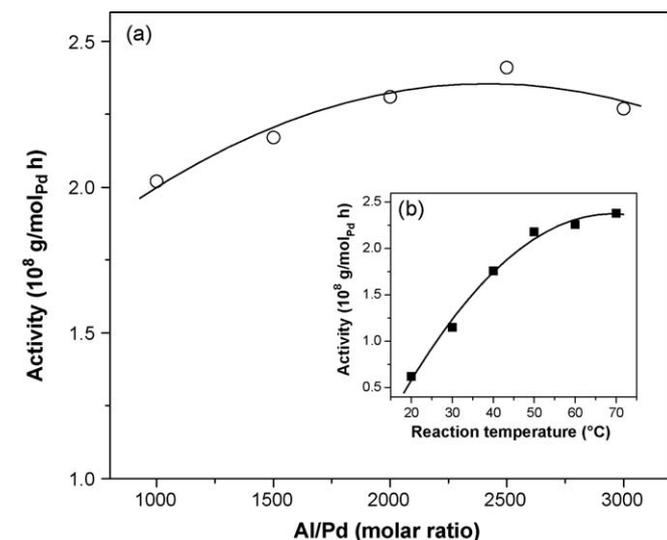


Fig. 4. Plot of activity vs. Al/Pd (molar ratio) and reaction temperature; 0.25 μmol **4c**, 4.14 g of norbornene feeds, $V_{\text{total}} = 30$ ml, 2 min polymerization run, Al/Pd = 2000 for (■) and 50 °C for (○).

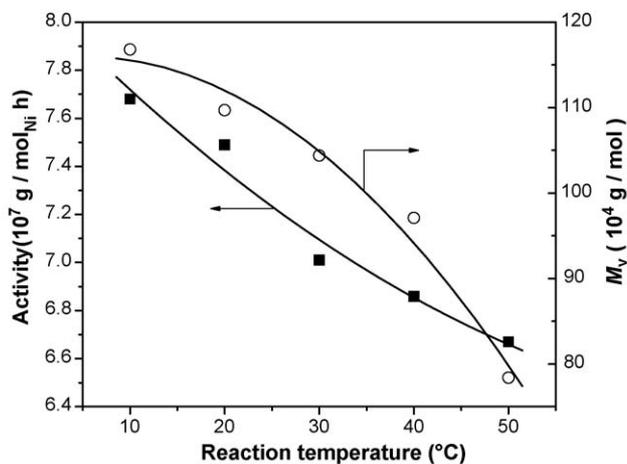


Fig. 5. Plot of activity and M_v vs. reaction temperature; 0.25 μmol **4a**, 3.31 g of norbornene feeds, Al/Ni = 2000, $V_{\text{total}} = 30$ ml, 5 min polymerization run.

As shown in Fig. 5, with the increase in the reaction temperature, both the catalytic activities and \bar{M}_v of the polymers decrease apparently. At 10 °C, the highest catalytic activity up to 7.68×10^7 g PNBE/(mol_{Ni} h) and \bar{M}_v up to 116.8×10^4 g/mol are obtained. However, for palladium precatalyst **4c**, with the increase in the reaction temperature, a significant increase in the catalytic activities is observed and the highest catalytic activity up to 2.38×10^8 g PNBE/(mol_{Pd} h) appears at 70 °C (Fig. 4(b)).

As shown in Fig. 6, the concentration of norbornene also considerably affects the polymerization. For nickel precatalyst **4a**, the catalytic activity and \bar{M}_v of the PNBEs display a nearly linear increase with the increase in the concentration of norbornene. For palladium precatalyst **4c**, the catalytic activity also increases with the increase in the concentration of norbornene; however, the monomer conversion increases initially and then gradually decreases (Fig. 7).

Since the effects of temperature on the polymerization performance show the different trends between the nickel complexes and palladium complexes, the comparative experiments of their catalytic activities were performed at 20–40 °C. As

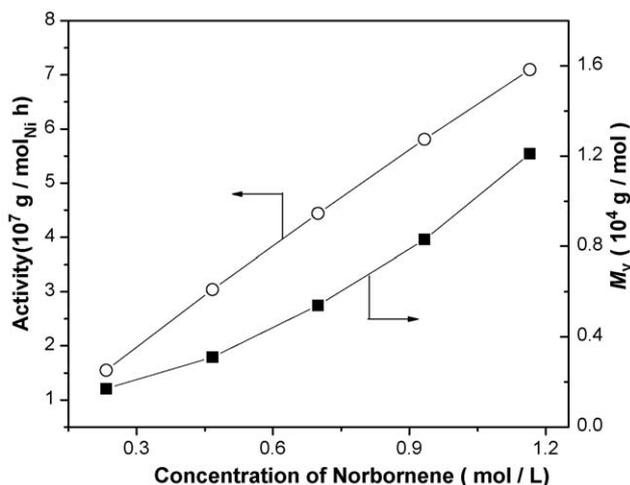


Fig. 6. Plot of activity and M_v vs. concentration of norbornene; 20 °C, 0.25 μmol **4a**, Al/Ni = 2000, $V_{\text{total}} = 30$ ml, 5 min reaction run.

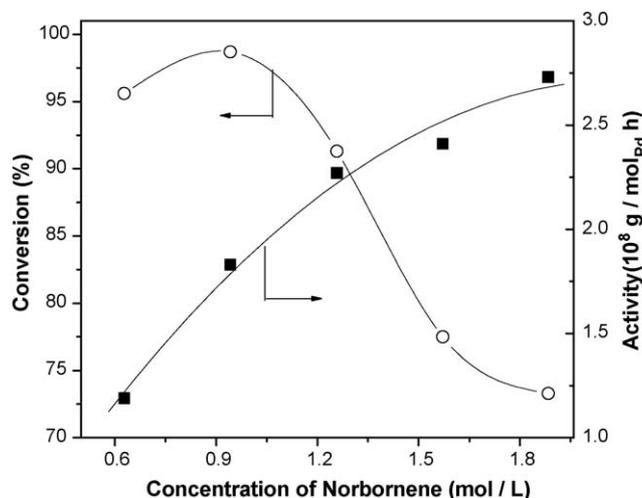


Fig. 7. Plot of activity and conversion vs. concentration of norbornene; 50 °C, 0.25 μmol of **4c**, Al/Pd = 2000, V_{total} = 30 ml, 2 min polymerization run.

shown in Table 4 (Entries 1, 5 and 6), precatalyst **4a** has higher activity than precatalyst **4c** (7.49×10^7 g PNBE/(mol_{Ni} h) versus 3.19×10^7 g PNBE/(mol_{Pd} h)) at 20 °C and the activity of precatalyst **4c** and precatalyst **4a** are comparable at 40 °C (7.29×10^7 g PNBE/(mol_{Pd} h) versus 7.01×10^7 g PNBE/(mol_{Ni} h)). Therefore, precatalyst **4a** has higher activity than precatalyst **4c** at low temperature. In contrast, the activity of precatalyst **4c** is higher at high temperature.

2.3. Analyses of polynorbornene

Norbornene can be polymerized by three means: ring-opening metathesis polymerization (ROMP), cationic polymerization and vinyl addition polymerization [37]. ROMP yields polynorbornene containing unsaturated double bond in the backbone. Cationic polymerization typically results in the formation of low molecular weight polymers with rearranged norbornene units in the backbone. Vinyl addition polymerization yields a completely saturated polynorbornene. As shown in Table 4, these polynorbornenes bear high glass transition temperature ranging from 316.0 to 325.0 °C. FTIR analyses display that no absorption is observed in the range of 1500–1600 cm^{-1} , which is characteristic of carbon–carbon double bonds; therefore these polynorbornenes are vinyl addition products in nature.

All PNBEs produced by employing these nickel complexes are soluble in chlorobenzene, *o*-dichlorobenzene and dichloroethylene, which indicates that they have low stereoregularities. However, the PNBEs produced by these palladium complexes are insoluble in usual solvents such as chloroform, chlorobenzene, dichlorobenzene, DMF, THF and DMSO. Therefore, the molecular weights of the polynorbornenes cannot be determined. For the purposes of comparison, the solid-state CPMAS-¹³C NMR spectra of polynorbornenes produced by palladium precatalyst and nickel complex are presented in Fig. 8(a and b), respectively. Both polynorbornenes again proved to be vinyl addition polymers in nature since no olefinic resonances are observed, which is in accord with the FTIR results. In addition,

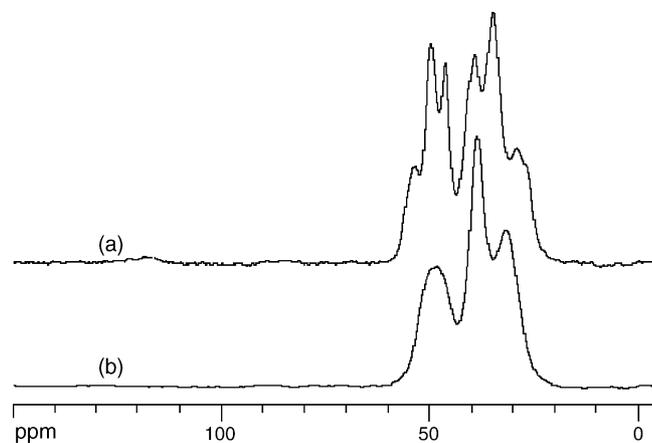


Fig. 8. Solid-state ¹³C NMR spectra of polynorbornenes produced by precatalysts **4c** (a) and **4a** (b).

tion, the PNBEs are *exo* enchainned because no resonances appear in the 20–24 ppm region, which has been taken as evidence of *endo* enchainment on the basis of model studies [38]. Despite these similarities, the ¹³C NMR spectra of the PNBEs are distinctly different in appearance, which indicates that there are differences in the microstructure of the PNBEs. Therefore, it is the high stereoregularity that leads to the insolubility of the PNBEs produced by palladium complexes.

It is noteworthy that the PNBEs obtained by using the binuclear nickel complexes display a slightly broader molecular weight distribution (PDI > 3.2, Entries 1–3 in Table 4) than the PNBEs (PDI < 1.6) obtained by using mononuclear salicylaldimine–Ni(II) complexes [23] under similar conditions. Presumably, the two different nickel units of complexes **4a**, **4b** or **8a** in structure create the two different active species, which directly leads to the broadening of the molecular weight distribution.

3. Conclusion

We have synthesized a series of binuclear salicylaldimine-based neutral nickel and palladium complexes and characterized their structures. For these complexes, each salicylaldimine derivative unit plays a role of a bulky group at C-3 position of the other unit. With MMAO as cocatalysts, these well-defined complexes and **4a** displayed higher catalytic activities than those of mononuclear salicylaldimine-based complexes reported previously. For salicylaldimine-based nickel complexes, the steric effect of substituents in the *ortho* position of the salicylaldiminato fragment is negligible in norbornene polymerization. However, this steric effect is noticeable for the corresponding palladium complexes. For salicylaldimine–palladium complexes, appropriately bulky groups in the *ortho* position of the salicylaldiminato fragment are responsible for their high catalytic activity. In addition, these palladium complexes with the pyridine ligand display much lower activities than their counterparts with the PPh₃ ligand. FTIR and ¹³C NMR analyses of the PNBEs show that norbornene polymerization proceeds with vinyl addition polymerization.

4. Experimental

4.1. General remarks and materials

All manipulations of air- and/or water-sensitive compounds were performed under a dry nitrogen atmosphere using standard Schlenk techniques. The NMR data of the ligands and the complexes were obtained on a Bruker 300 MHz spectrometer at ambient temperature, with CDCl_3 or C_6D_6 as the solvents. The ^{13}C NMR spectra of the polynorbornenes obtained with nickel precatalysts were recorded on a Varian Unity-400 MHz spectrometer with *o*-dichlorobenzene as the solvent at ambient temperature. Solid-state ^{13}C CP/MAS (cross-polarization with magic angle spinning) NMR spectra of the polynorbornenes obtained with palladium precatalysts were obtained on a Varian Unity Plus NMR spectrometer operating at 100 MHz. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a heating rate of $10^\circ\text{C}/\text{min}$. The weight-average molecular weights (\overline{M}_w) and the polydispersity indices (PDI) of the polynorbornene samples were determined via high temperature GPC according to the procedure reported previously [39]. Elemental analyses were performed on a Perkin-Elmer Series II CHN/O analyzer 2400. Viscosity-average molecular weights were calculated from the intrinsic viscosity by using the Mark–Houwink coefficients: $\alpha = 0.56$, $K = 5.97 \times 10^{-4} \text{ dl g}^{-1}$ [40].

Benzene, *n*-pentane and tetrahydrofuran were refluxed with sodium/benzophenone ketyl and were distilled under nitrogen prior to use. Chlorobenzene and dichloromethane were dried over CaH_2 and distilled before use. Triphenylphosphine, sodium tetrachloropalladate(II) and tetramethyltin were obtained from Aldrich and used without further purification. Pyridine was dried over sodium hydroxide and distilled prior to use. Norbornene was purchased from Aldrich and dried over sodium before use. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. 2,6-Diisopropylaniline and NaH were purchased from Acros. *trans*-[Ni(PPh₃)₂PhCl] [41] and (1,5-cycloioctadene)PdMeCl [(COD)PdMeCl] [42,43] were prepared according to the analogous methods reported, respectively. Compounds **1a**, **5** [44] and complex **4a** [33] were synthesized according to the literature procedures.

4.2. Synthesis of compounds **1b** and ligands **2b**, **6**

1b: Compound **1a** (2.42 g, 10 mmol) was added cautiously with cooling in ice and salt, to a mixture of concentrated sulphuric acid (2 ml) and concentrated nitric acid (1 ml). After 30 min the nitration mixture was poured on ice, and the yellow product was washed with ice-water, dried and crystallized from THF, giving 2.4 g (72%) of product as a pale yellow powder. ^1H NMR (DMSO): δ 10.4 (s, 2H, =CHO), 8.43 (d, $^3J = 3 \text{ Hz}$, 2H, Ar–H), 8.50 (d, $^3J = 3 \text{ Hz}$, 2H, Ar–H), 4.04 (br, ^1H , OH). MS(EI): m/z 332(M^+). Anal. calcd. for $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_8$: C, 50.61; H, 2.43; N, 8.43. Found: C, 50.34; H, 2.47; N, 8.38.

2b: To a stirred solution of compound **1b** (1.66 g, 5 mmol) in dried methane dichloride (30 ml) were added 2,6-diisopropylaniline (2.22 g, 12.5 mmol) and formic acid (0.1 ml) as a catalyst. The mixture was refluxed and stirred for 24 h. The evaporation of solvent gave a yellow solid powder as the crude product. Recrystallization from CHCl_3 -EtOH or chloroform-ethanol gave 3.0 g (92%) of **2b** as yellow needle crystals. ^1H NMR (CDCl_3): δ 1.24 (d, $^3J = 6.6 \text{ Hz}$, 24H, CH_3), 2.99 (sept, $^3J = 6.6 \text{ Hz}$, 4H, CH), 7.27 (s, 6H, Ar–H), 8.45 (d, $^3J = 2.7 \text{ Hz}$, 2H, Ar–H), 8.47 (s, 2H, CH=N), 8.66 (d, $^3J = 2.7 \text{ Hz}$, 2H, Ar–H), 15.1 (s, 2H, OH). Anal. calcd. for $\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_6$: C, 70.13; H, 6.51; N, 8.61. Found: C, 69.83; H, 6.48; N, 8.57.

Ligand **6**: Ligand **6** was obtained as yellow powder in 99% yield, by the method analogous to that for the synthesis of ligand **2b**. ^1H NMR (CDCl_3): δ 1.18 (d, $^3J = 6.8 \text{ Hz}$, 12H, CH_3), 1.19 (d, $^3J = 6.8 \text{ Hz}$, 12H, CH_3), 3.09 (m, $^3J = 6.8 \text{ Hz}$, 4H, CH), 7.20 (s, 6H, Ph–H), 7.42 (m, 6H, Ar–H), 7.95 (d, 2H, Ar–H), 8.18 (s, 2H, Ar–H), 8.60 (s, 2H, CH=N), 12.7 (s, 2H, OH). Anal. calcd. for $\text{C}_{46}\text{H}_{48}\text{N}_2\text{O}_2$: C, 83.60; H, 7.32; N, 4.24. Found: C, 83.37; H, 7.27; N, 4.18.

4.3. Synthesis of complexes **4b** and **8a**

4b: A solution of **2b** (0.49 g, 0.76 mmol) in anhydrous THF (15 ml) was added to sodium hydride (46 mg, 1.9 mmol). The resultant mixture was stirred at room temperature for 4 h, then filtered and evaporated. The resultant solid residue and *trans*-[Ni(PPh₃)₂PhCl] (1.06 g, 1.52 mmol) were dissolved in THF (40 ml) in a Schlenk flask and stirred at room temperature for 14 h. The resultant mixture was filtered, and the filtrate was concentrated in vacuum to ca. 6 ml. Pentane (30 ml) was then added. A brown solid precipitated from solution and was isolated by filtration to yield 0.37 g (34%) of **4b**. ^1H NMR (C_6D_6): δ 1.26 (d, $J_{\text{HH}} = 6.7 \text{ Hz}$, 12H, CH_3), 1.38 (d, $J_{\text{HH}} = 6.6 \text{ Hz}$, 12H, CH_3), 4.02 (m, 4H, CH), 6.77–7.89 (m, 46H, Ar–H), 8.14 (d, 2H, $J_{\text{HP}} = 9.3 \text{ Hz}$, N=CH), 8.35 (d, 4H, Ar–H); ^{13}C NMR (C_6D_6): δ 23.1, 23.7, 25.3, 25.6, 28.4, 29.1, 116.0, 117.4, 118.9, 119.3, 120.6, 124.4, 126.6, 128.9, 129.8, 132.8, 134.1, 135.8, 136.0, 138.8, 140.5, 142.9, 148.4, 150.7, 168.3. Anal. calcd. for $\text{C}_{86}\text{H}_{80}\text{N}_4\text{Ni}_2\text{O}_6\text{P}_2$: C, 71.49; H, 5.58; N, 3.88. Found: C, 71.85; H, 5.55; N, 3.91.

8a: Complex **8a** was obtained as red-brown powder in 37% yield, following the method analogous to that for the synthesis of **4b**. ^1H NMR (300 MHz, C_6D_6): δ 1.29 (d, $J_{\text{HH}} = 6.5 \text{ Hz}$, 12H, CH_3), 1.36 (d, $J_{\text{HH}} = 6.5 \text{ Hz}$, 12H, CH_3), 4.13 (m, 4H, CH), 6.12–7.94 (m, 54H, Ar–H), 8.07 (s, 2H, Ar–H), 8.18 (s, 2H, N=CH); ^{13}C NMR (C_6D_6): δ 23.8, 25.9, 28.4, 114.2, 118.9, 121.4, 123.2, 124.7, 125.4, 129.5, 131.1, 133.0, 133.8, 135.3, 136.1, 136.9, 137.6, 138.3, 141.1, 144.6, 150.6, 164.3, 168.6. Anal. calcd. for $\text{C}_{94}\text{H}_{86}\text{N}_2\text{Ni}_2\text{O}_2\text{P}_2$: C, 77.59; H, 5.96; N, 1.93. Found: C, 77.29; H, 5.93; N, 1.98.

4.4. Synthesis of binuclear palladium complexes **4c–f** and **8b** and **8c**

A solution of **2a** (0.28 g, 0.5 mmol) in anhydrous THF (15 ml) was added to sodium hydride (48 mg, 2 mmol). The resultant

mixture was stirred at room temperature for 4 h, then filtered and evaporated. The solid residue was dissolved in 15 ml of benzene to form a clear orange solution. The solution was transferred to a Schlenk flask containing 0.265 g of (COD)PdMeCl (1 mmol) and 20 ml of benzene. The mixture was stirred at room temperature for 15 min and then 0.262 g PPh₃ (1 mmol) was added. The resulting mixture was stirred at room temperature overnight and filtrated. The filtrate was concentrated in vacuum to ca. 6 and 30 ml of pentane was slowly added. 0.54 g of **4c** was given as deep yellow flakes in 83% yield. The other palladium complexes **4d–f**, **8b** and **8c** were prepared via similar procedures.

4c: ¹H NMR (C₆D₆): δ 0.01 (d, J_{PH} = 3.6 Hz, 6H, Pd–CH₃), 1.01 (d, J_{HH} = 6.9 Hz, 12H, –CH₃), 1.12 (d, J_{HH} = 6.9 Hz, 12H, –CH₃), 2.95 (m, 4H, –CH), 6.56–7.96 (m, 42H, Ar–H), 8.02 (s, 2H, N=CH); ¹³C NMR (C₆D₆): δ 3.61 (d, Pd–CH₃), 23.2, 23.7, 25.1, 25.6(–CH₃), 28.4, 29.1 (–CH), 118.8, 121.6, 123.5, 129.1, 127.8, 128.6, 129.1, 129.9, 130.4, 132.0, 133.6, 134.1, 137.0, 137.4, 143.5, 143.5, 167.9 (N=C). Anal. calcd. for C₇₆H₇₈N₂O₂P₂Pd₂: C, 68.83; H, 5.93; N, 2.11. Found: C, 69.07; H, 5.88; N, 2.16.

4d (78%): The reaction was carried out according to the same procedure as for **4c**, except that pyridine (5 equivalents) was used instead of triphenylphosphine. ¹H NMR (C₆D₆): δ 0.19 (s, 6H, Pd–CH₃), 0.90 (d, J_{HH} = 6.6 Hz, 24H, –CH₃), 2.85 (m, 4H, –CH), 6.66–7.85 (m, 22H, Ar–H + Py–H), 8.21 (d, 2H, N=CH); ¹³C NMR (C₆D₆): δ 1.63 (Pd–CH₃), 23.1, 24.7, 25.4 (–CH₃), 28.2, 29.1 (–CH), 120.9, 121.7, 122.5, 125.9, 127.3, 126.4, 136.6, 139.8, 146.3, 150.3, 152.4, 169.4 (N=C). Anal. calcd. for C₅₀H₅₈N₄O₂Pd₂: C, 62.56; H, 6.09; N, 5.84. Found: C, 62.94; H, 6.04; N, 5.76.

4e (74%): The reaction was carried out according to the same procedure as for **4c**, except that CH₂Cl₂ was used instead of benzene. ¹H NMR (C₆D₆): δ 0.22 (d, J_{PH} = 3.3 Hz, 6H, Pd–CH₃), 1.21 (d, J_{HH} = 6.8 Hz, 12H, –CH₃), 1.42 (d, J_{HH} = 6.7 Hz, 12H, –CH₃), 3.73 (m, 4H, –CH), 7.18–7.79 (m, 40H, Ar–H), 8.13 (d, 2H, J_{HP} = 3 Hz, N=CH); ¹³C NMR (C₆D₆): δ 3.88 (d, Pd–CH₃), 23.1, 23.7, 24.9, 25.2 (–CH₃), 28.7, 29.5 (–CH), 119.4, 123.6, 123.9, 130.1, 130.8, 130.9, 131.1, 131.6, 132.6, 134.0, 134.6 (d, J_{CP} = 15 Hz), 135.1, 141.0, 141.4, 147.5, 147.7, 164.2, 166.8 (N=C). Anal. calcd. for C₇₆H₇₆N₄O₆P₂Pd₂: C, 64.45; H, 5.41; N, 3.96. Found: C, 64.28; H, 5.37; N, 3.94.

4f (87%): The reaction was carried out according to the same procedure as for **4e**, except that pyridine (5 equivalents) was used instead of triphenylphosphine. ¹H NMR (C₆D₆): δ 0.42 (s, 6H, Pd–CH₃), 1.11 (d, J_{HH} = 6.9 Hz, 12H, –CH₃), 1.48 (d, J_{HH} = 6.9 Hz, 12H, –CH₃), 3.69 (m, 4H, –CH), 6.47–8.33 (m, 20H, Ar–H + Py–H), 8.72 (d, 2H, J_{HP} = 3.1 Hz, N=CH); ¹³C NMR (C₆D₆): δ 1.02 (Pd–CH₃), 23.1, 24.9, 25.1 (–CH₃), 28.4, 29.2 (–CH), 123.9, 124.3, 124.6, 127.9, 128.2, 128.5, 137.9, 140.8, 147.5, 151.3, 152.1, 167.7 (N=C). Anal. calcd. for C₅₀H₅₆N₆O₆Pd₂: C, 57.20; H, 5.38; N, 8.00. Found: C, 57.38; H, 5.32; N, 7.93.

8b (83%): Mauve crystals. ¹H NMR (C₆D₆): δ 0.18 (d, J_{PH} = 3.4 Hz, 6H, Pd–CH₃), 1.21 (d, J_{HH} = 6.8 Hz, 6H, –CH₃), 1.31 (d, J_{HH} = 6.7 Hz, 6H, –CH₃), 1.32 (d, J_{HH} = 6.8 Hz, 6H, –CH₃), 1.57 (d, J_{HH} = 6.8 Hz, 6H, –CH₃), 3.74 (m, 2H, –CH), 4.20 (m, 2H, –CH), 6.76–7.74 (m, 46H, Ar–H), 8.28 (d, 2H,

J_{HP} = 11.3 Hz, N=CH); ¹³C NMR (C₆D₆): δ 2.97 (d, J_{CP} = 42 Hz, Pd–CH₃), 23.3, 23.1, 25.7, 25.1(–CH₃), 28.7 (–CH), 119.8, 123.7, 124.0, 125.3, 126.6, 126.8, 129.0, 129.8, 132.1, 132.7, 134.5 (d, J_{CP} = 45 Hz), 138.5, 139.4, 141.3, 141.9, 148.8, 168.9 (N=C). Anal. calcd. for C₈₄H₈₂N₂O₂P₂Pd₂: C, 70.73; H, 5.79; N, 1.96. Found: C, 70.49; H, 5.83; N, 2.03.

8c (81%): Pink powder. ¹H NMR (C₆D₆): δ 0.29 (s, 6H, Pd–CH₃), 1.04 (d, J_{HH} = 6.8 Hz, 6H, –CH₃), 1.18 (d, J_{HH} = 6.8 Hz, 6H, –CH₃), 1.33 (d, J_{HH} = 6.8 Hz, 6H, –CH₃), 1.37 (d, J_{HH} = 6.8 Hz, 6H, –CH₃), 3.71 (m, 4H, –CH), 6.29 (t, 4H, Py–H), 6.71 (t, 2H, Py–H), 6.93 (m, 4H, Py–H), 7.24 (s, 6H, Ph–H), 7.70 (t, 6H, Ar–H), 8.06 (s, 2H, CH=N), 8.35 (dd, 4H, 1.2 Hz, Ar–H); ¹³C NMR (C₆D₆): δ –0.86 (s, Pd–CH₃), 21.5, 21.6, 23.5, 23.6, 26.6, 26.8, 118.8, 122.2, 123.4, 123.8, 125.6, 127.7, 134.6, 135.3, 138.6, 139.8, 148.0, 150.7, 166.7 (N=C). Anal. calcd. for C₅₈H₆₂N₄O₂Pd₂: C, 65.72; H, 5.90; N, 5.29. Found: C, 65.86; H, 5.86; N, 5.24.

4.5. Typical polymerization procedure

To a 100 ml Schlenk flask with a mechanical stirrer were added the following materials under inert gas atmosphere in the order given: a solution of norbornene (44 mmol, 4.14 g) in C₆H₅Cl (6 ml), **4c** (0.25 μmol) dissolved in C₆H₅Cl (1 ml) and 22.3 ml of C₆H₅Cl. The reaction was started by the addition of 0.75 ml of a MMAO solution (1.5 mmol in heptane) at 50 °C. After vigorous stirring for 2 min, the reaction mixture was poured into 200 ml of acidic EtOH (EtOH–HCl_{conc} = 50/1). The polymer was isolated by filtration, washed with EtOH and dried under vacuum at 80 °C for 10 h.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 286028 and 286029 for complexes **4e** and **8b**, 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.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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