## **ORGANOMETALLICS**

# Synthesis, Structures, and Norbornene Polymerization Behavior of Imidazo[1,5-a]pyridine-sulfonate-Ligated Palladacycles

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**S** Supporting Information

**ABSTRACT:** Two imidazo[1,5-*a*]pyridine-sulfonate proligands, L1 and L2, were synthesized in five-step reactions. Treatment of the proligands with palladacycles {[Pd(OAc)(8-Me-quin-H)]<sub>2</sub>, [Pd(dmba)( $\mu$ -Cl)]<sub>2</sub>, and [Pd(*o*-acetanilido)-( $\mu$ -trifluoroacetato)]<sub>2</sub>} yielded the desired five-membered C(sp<sup>3</sup>),N-chelated (Pd1, Pd2), C(sp<sup>2</sup>),N-chelated (Pd3, Pd4), and six-membered C(sp<sup>2</sup>),O-chelated (Pd5, Pd6) palladacycles, respectively. All these complexes were fully



characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR, high-resolution mass spectrometry, and elemental analysis. The molecular structures of complexes Pd1, Pd2, Pd4, and Pd5 were determined by single-crystal X-ray diffraction analysis. In the presence of MAO or Et<sub>2</sub>AlCl, Pd1–Pd6 exhibited activities toward the addition polymerization of norbornene which decreased in the order Pd6 > Pd5 > Pd4 > Pd2 > Pd3 > Pd1. The Pd1–Pd6/MAO catalytic system showed high thermal stability and reached the highest activity at 100 °C ( $6.0 \times 10^7$  g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup> with 99.9% conversion). In the presence of Et<sub>2</sub>AlCl with low loading (100 equiv), Pd5 and Pd6 exhibited high activities (up to 2.9 × 10<sup>7</sup> g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup> with 96.5% conversion). It was demonstrated that the structures of palladacycles and the substituents on the ligands significantly affected the activities of these complexes.

#### INTRODUCTION

The vinyl addition polymer of norbornene (PNB) is an unique material, owing to its high chemical resistance, good UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, large refractive index, and low birefringence.<sup>1</sup> Therefore, PNB has been applied to the microelectronic devices and LCD protective coating and has been used as a high-temperature-resistant protective material, which has attractive business prospects.<sup>2</sup>

Palladium(II) complexes bearing phosphine-sulfonate ligands ({PO}, Chart 1, I) exhibit unique characteristics in

### Chart 1. Phosphine-sulfonate and NHC-sulfonate Complexes



olefin polymerization.<sup>3</sup> {PO}Pd(R)(L) species (L = labile ligand) can polymerize ethylene to linear polyethylene and copolymerize ethylene with several unprecedented types of polar monomers including acrylates, vinyl acetate, acrylonitrile, and carbon monoxide to functionalized linear polymers.<sup>3,4</sup> The outstanding behavior of {PO}Pd species results from their electronic asymmetry that may inhibit  $\beta$ -H and  $\beta$ -X eliminations, thus enabling the generation of linear polymers. The cis arrangement of the phosphine ligand, a strong donor, and the sulfonate ligand, a very weak donor, plays an important role here.<sup>4</sup>

Since first reported by Arduengo and co-workers in 1991, *N*-heterocyclic carbenes (NHCs) have been widely employed in catalysis due to their distinctive capabilities.<sup>5,6</sup> However, successful applications of NHC-derived transition metal complexes for olefin polymerizations are rather rare so far.<sup>7,8c-h</sup> As donors stronger than typical phosphines, NHCs can be used as substitutes for the phosphines. The chelating NHC-sulfonate ligands may possess enhanced electronic asymmetry and lower metal electrophilicity and thus are potential candidates as ancillary ligands for late transition-metal olefin polymerization catalysts. In 2009, Nozaki et al. reported two methyl palladium complexes in which the NHC and sulfonate units were linked by a methylene spacer (Chart

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1, II),<sup>8a</sup> but their catalytic properties for olefin polymerization has not been investigated. Similar seven-membered chelating palladium(II) complexes containing saturated or unsaturated ortho-NHC-arenesulfonate (NHC-sulfonate) ligands were synthesized by Jordan's group<sup>8b</sup> and our group,<sup>8c,d</sup> respectively (Chart 1, III). Neither saturated nor unsaturated NHCsulfonate Pd(II) complexes showed activity for ethylene polymerization. Nevertheless, the unsaturated NHC-sulfonate Pd(II) complexes had been demonstrated active in norbornene polymerization in the presence of methylaluminoxane (MAO).<sup>8c,d</sup> Recently, Nozaki et al.<sup>8e-h</sup> reported a series of Ni(II) and Pd(II) complexes bearing six-membered chelating imidazo [1,5-a]quinolin-9-olate-1-ylidene (IzQO) ligands (Chart 1, IV), which showed high activities for ethylene polymerization and copolymerization with some polar monomers. As one of the few successful demonstrations of NHC-based ligands for olefin polymerization, the Pd/IzQO system highlighted the significance of the rigid skeleton. Stimulated by these strategies,<sup>8</sup> we speculated that an imidazo[1,5-a]pyridine-sulfonate ligand would serve as a promising ligand, owing to its electronic asymmetry and sixmembered chelating rigid backbone.

Imidazo[1,5-*a*]pyridines have attracted extensive attention due to their bicyclic nature.<sup>9</sup> The electronic and steric effects can be well tuned by modifiable substituents on the nitrogen atom. Thus far, the transition-metal complexes containing the imidazo[1,5-*a*]pyridine ligand have been widely studied and applied to various catalytic reactions,<sup>10</sup> but few examples for catalytic olefin polymerization. To date, the imidazo[1,5-*a*]pyridine-sulfonate ligands and their transition metal complexes have not been reported.

Since the first synthesis by Cope and Siekman in 1965,<sup>11</sup> palladacycles have become an important class of catalysts on account of their versatile frameworks, extraordinary catalytic activity, synthetically easy accessibility, extra stability toward air and moisture, and relatively low toxicity.<sup>12</sup> Despite a wide variety of heteroatom-derived palladacycles being synthesized and utilized in catalytic hydrogenation reactions, coupling reactions, the Aldol reaction, and other organic reactions,<sup>13</sup> reports on palladacycles with NHCs are rather limited.<sup>14</sup> Recently, we reported that aryloxide-NHC-ligated palladacycles exhibited high catalytic activities in the vinyl polymerization of norbornene.<sup>8c,15f-h</sup>

Inspired by the above research, we believe the imidazo[1,5-a]pyridine-sulfonate-ligated palladacycles, combining the electronic effects of the ligands and the stability of the palladacycles, should be regarded as polymerization catalysts. Herein, we report the synthesis and structures of a series of C(sp<sup>3</sup>),N-chelated, C(sp<sup>2</sup>),N-chelated, and C(sp<sup>2</sup>),O-chelated imidazo[1,5-a]pyridine-sulfonate palladacycles and their performances in the vinyl polymerization of norbornene upon activation with either diethylaluminum chloride (Et<sub>2</sub>AlCl) or methylaluminoxane (MAO).

#### RESULTS AND DISCUSSION

**Synthesis of Proligands.** Proligands L1 and L2 were synthesized in five-step reactions from commercially available 2,6-dibromopyridine (Scheme 1). Both the proligands were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and high-resolution mass spectrometry (HRMS). Their <sup>1</sup>H NMR spectra exhibited singlets at 9–10 ppm characteristic for the imidazole, consistent with those reported in the literature for similar imidazole salts.<sup>15</sup>





Synthesis of Palladacycles.  $C(sp^3)$ ,N-chelated palladacycles Pd1 and Pd2,  $C(sp^2)$ ,N-chelated palladacycles Pd3 and Pd4, and  $C(sp^2)$ ,O-chelated palladacycles Pd5 and Pd6 were synthesized by the reactions of proligands L1 and L2 with  $[Pd(OAc)(8-Me-quin-H)]_2$  (8-Me-quin-H = 8-CH<sub>2</sub>-quinoline),  $[Pd(dmba)(\mu$ -Cl)]<sub>2</sub> (dmba = Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), and  $[Pd(o\text{-acetanilido})(\mu\text{-trifluoroacetato})]_2$  (acetanilido =  $C_6H_4$ NHCOCH<sub>3</sub>), respectively (Scheme 2). All of these





palladacycles are stable in air and moisture. They have been fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, HRMS, and elemental analysis. In their <sup>1</sup>H NMR spectra, the signals of the imidazole proton at the C-2 position for the proligands completely disappeared. The signals of the carbene carbons in <sup>13</sup>C NMR spectra supported their structures (158.0 ppm for Pd1; 157.4 ppm for Pd2; 161.1 ppm for Pd3; 158.4 ppm for Pd4; 154.8 ppm for Pd5; 154.9 ppm for Pd6).

The molecular structures of Pd1, Pd2, Pd4, and Pd5 were determined by single-crystal X-ray diffraction analysis. As shown in Figures 1–4, they all possess spiro structures with palladium as the spiroatom. Complexes Pd1, Pd2, and Pd4 each contain a six-membered  $\{C-O\}Pd$  chelate ring and a five-membered C,N-chelated palladacycle, while complex Pd5 consists of two six-membered chelate rings. The Pd–N bond lengths in C(sp<sup>3</sup>),N-chelated palladacycles (2.0655(14) Å for Pd1, 2.058(2) Å for Pd2) are shorter than the sum of the covalent radii of the Pd and N atoms (2.10 Å).<sup>16</sup> However, the



Figure 1. ORTEP diagram of Pd1. Thermal ellipsoids are shown at the 60% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): Pd(1)-C(17) 2.0109(16), Pd(1)-C(1) 2.0238(17), Pd(1)-N(1) 2.0655(14), Pd(1)-O(1) 2.1773(13), C(17)-Pd(1)-C(1) 97.10(6), C(17)-Pd(1)-N(1) 178.97(6), C(1)-Pd(1)-N(1) 83.02(6), C(17)-Pd(1)-O(1) 88.35(5), C(1)-Pd(1)-O(1) 174.44(5), N(1)-Pd(1)-O(1) 91.51(5).



Figure 2. ORTEP diagram of Pd2. Thermal ellipsoids are shown at the 60% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): Pd(1)-O(1) 2.1976(16), Pd(1)-N(3) 2.058(2), Pd(1)-C(7) 2.005(2), Pd(1)-C(18) 2.023(2), N(3)-Pd(1)-O(1) 92.05(7), C(7)-Pd(1)-O(1) 89.01(8), C(7)-Pd(1)-N(3) 178.11(8), C(7)-Pd(1)-C(18) 95.77(9), C(18)-Pd(1)-O(1) 173.89(8), C(18)-Pd(1)-N(3) 83.07(9).

Pd–N bond length (2.1149(9) Å) in C(sp<sup>2</sup>),N-chelated palladacycle Pd4 and the Pd–O(palladacycle) bond length (2.063(8) Å) in C(sp<sup>2</sup>),O-chelated palladacycle Pd5 are slightly longer than the sum of the covalent radii of the Pd and N atoms and of the Pd and O atoms (2.05 Å), respectively.<sup>16</sup> The different bond lengths indicated that the coordination of Pd and heteroatom on the palladacycles in Pd1 and Pd2 were stronger than those in Pd4 and Pd5. In addition, the Pd–C(sp<sup>3</sup>) bonds (2.0238(17) Å for Pd1, 2.023(2) Å for Pd2) are evidently longer than the Pd–C(sp<sup>2</sup>)



Figure 3. ORTEP diagram of Pd4. Thermal ellipsoids are shown at the 60% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): Pd(1)-C(18) 1.9754(10), Pd(1)-C(1) 2.0067(9), Pd(1)-N(3) 2.1149(9), Pd(1)-O(1) 2.1788(8), C(18)-Pd(1)-C(1) 97.91(4), C(18)-Pd(1)-N(3) 81.71(4), C(1)-Pd(1)-N(3) 168.91(3), C(18)-Pd(1)-O(1) 171.83(3), C(1)-Pd(1)-O(1) 88.84(3), N(3)-Pd(1)-O(1) 92.54(3).



Figure 4. ORTEP diagram of Pd5. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): Pd(1)-O(1) 2.173(7), Pd(1)-O(4) 2.063(8), Pd(1)-C(7) 1.974(10), Pd(1)-C(17) 1.974(10), O(4)-Pd(1)-O(1) 90.0(3), C(7)-Pd(1)-O(1) 89.0(3), C(7)-Pd(1)-O(4) 167.7(4), C(17)-Pd(1)-O(1) 170.3(4), C(17)-Pd(1)-O(4) 89.5(4), C(17)-Pd(1)-C(7) 93.5(4).

bonds (1.9754(10) Å for Pd4, 1.974(10) Å for Pd5). It should be noted that the Pd–O(SO<sub>3</sub>) bond lengths (in the range of 2.173(7)–2.1976(16) Å) are analogous to that of reported NHC-sulfonate Pd(II) complexes (in the range of 2.1442(12)–2.182(2) Å, Chart 1, III)<sup>8b,c</sup> and {PO}Pd(II) complexes (2.159 Å, Chart 1, I).<sup>3</sup> The Pd–C(NHC) bond lengths are similar in all complexes (2.0109(16) Å for Pd1, 2.005(2) Å for Pd2, 2.0067(9) Å for Pd4, and 1.974(10) Å for Pd5), approaching that of reported NHC-sulfonate Pd(II) complexes (~1.98 Å)<sup>8c</sup> but definitely shorter than Pd–P bond length (2.199(2)–2.2841(12) Å) in {PO}Pd(II) complexes.<sup>3,m</sup> These results revealed that the coordination abilities of the imidazo[1,5-*a*]pyridine-sulfonate ligands are close to that of the NHC-sulfonate ligands and are slightly stronger than that of the {PO} ligands, because the tendency of the metal– ligand interaction is usually represented by the length of the metal–ligand bonds. In Pd1 and Pd2, the quinoline rings are perpendicular to the aromatic rings on the ligands, while Pd4 and Pd5 exhibit  $\pi-\pi$  stacked arrangements of their phenyl groups on the palladacycles and the aryl backbone on the ligands. From the decomposition temperatures of these complexes (Pd1, 250 °C; Pd2, 240 °C; Pd5, 236 °C; Pd4, 203 °C), it seems that Pd1 and Pd2 with vertical structures are more thermally stable than Pd4 and Pd5 with  $\pi-\pi$  stacking structures. These structural differences are hypothesized to influence the catalytic properties of these palladium catalysts in norbornene polymerization.<sup>17</sup>

**Norbornene Polymerization.** Recently, some nickel and palladium complexes containing NHC ligands have proved highly active catalysts for addition polymerization of norbornene.<sup>7,8c,d,15</sup> In order to explore the potential application of these imidazo[1,5-*a*]pyridine-sulfonate pallada-cycles, the catalytic behaviors of complexes Pd1–Pd6 toward norbornene polymerization were studied. First, no polymer was obtained in the absence of cocatalyst. For the purposes of determining the most suitable cocatalyst, both MAO and Et<sub>2</sub>AlCl were examined for norbornene polymerization.

MAO has excellent performance in many olefin polymerization systems.<sup>1,15</sup> Therefore, we first choose MAO as a cocatalyst for the experiment. Complex **Pd6** was employed as a precatalyst for the study of the polymerization in detail (Table 1). On activation with 2000 equiv of MAO, the activity of **Pd6** 

Table 1. Vinyl Polymerization of Norbornene with Pd1– Pd6 Activated by  $MAO^a$ 

entry	cat.	$T(^{\circ}C)$	Al/Pd	t (min)	conv. (%)	activity <sup>b</sup>
1	Pd6	40	2000	1	20.0	12.0
2	Pd6	60	2000	1	73.0	43.8
3	Pd6	80	2000	1	82.7	49.6
4	Pd6	100	2000	1	99.9	60.0
5	Pd6	120	2000	1	83.7	50.2
6	Pd6	140	2000	1	83.2	49.9
7	Pd6	100	1500	1	57.2	34.3
8	Pd6	100	1000	1	trace	
9	Pd5	100	2000	1	92.6	55.6
10	Pd4	100	2000	1	91.3	54.8
11	Pd3	100	2000	1	8.0	4.8
12	Pd3	100	2000	3	20.0	4.0
13	Pd2	100	2000	1	71.3	42.8
14	Pd1	100	2000	1	trace	
15	Pd1	100	2000	3	9.6	1.9

<sup>*a*</sup>Conditions: Pd complexes, 1  $\mu$ mol; solvent, 1,2-dichlorobenzene;  $V_{\text{totab}}$  10 mL; norbornene, 1.0 g; MAO, 1.5 M in toluene. <sup>*b*</sup>In units of 10<sup>6</sup> g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup>.

was relatively low  $(12.0 \times 10^6 \text{ g of PNB} \text{ (mol of Pd)}^{-1} \text{ h}^{-1})$ when the temperature was below 60 °C, but it increased to high levels in a wide range of temperatures from 60 to 140 °C, with the best activity at 100 °C ( $60.0 \times 10^6 \text{ g of PNB}$  (mol of Pd)<sup>-1</sup> h<sup>-1</sup>) (entries 1–6, Table 1). Pd6 can catalyze norbornene polymerization quantitatively in 1 min at an Al/ Pd ratio of 2000 at 100 °C. It proved that Pd6 has good thermal stability and still has high activities above 100 °C in the presence of MAO. The high temperature tolerance makes it possible for these complexes to be used in industry. Reducing the Al/Pd ratio from 2000 to 1500 caused the activity to decrease significantly (entry 7, Table 1). If we reduce the Al/Pd ratio to 1000, then only trace polymer could be observed. With the optimal conditions in hand, we continued testing the catalytic properties of the other five palladacycles. Similarly, complexes Pd5 and Pd4 also exhibited excellent polymerization activities ((54.8-55.6)  $\times$  10<sup>6</sup> g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup>) and conversions (91.3–92.6%) for the polymerization of norbornene (entries 9 and 10, Table 1). Pd2 showed moderate activity  $(42.8 \times 10^6 \text{ g of PNB} \text{ (mol of }$ Pd)<sup>-1</sup> h<sup>-1</sup>), with 71.3% conversion (entry 13, Table 1), while complexes Pd3 and Pd1 displayed obvious lower activities, as the highest activity was only  $4.8 \times 10^6$  g of PNB (mol of Pd)<sup>-1</sup>  $h^{-1}$  (entries 11, 12, 14, and 15, Table 1). The conversions did not significantly improve even if the reaction time was extended to 3 min (20.0% for Pd3, entry 11, and 9.6% for Pd1, entry 14; Table 1). The results showed that the activities of these six complexes decreased in the order of Pd6 > Pd5 > Pd4 > Pd2 > Pd3 > Pd1.

For different palladacycles containing the same ligand, C(sp<sup>2</sup>),O-chelated six-membered palladacycles (Pd5 and Pd6) were more active than the  $C(sp^2)$ ,N-chelated five-membered palladacycles (Pd3 and Pd4), and the latter were more active than the  $C(sp^3)$ , N-chelated five-membered palladacycles (Pd1 and Pd2). That is to say, for Pd2, Pd4, and Pd6, all containing a *tert*-butyl substituent, the order of activity is Pd6 ( $60.0 \times 10^6$ g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup>) > Pd4 (54.8  $\times$  10<sup>6</sup> g of PNB  $(mol of Pd)^{-1} h^{-1} > Pd2 (42.8 \times 10^6 g of PNB (mol of Pd)^{-1})$  $h^{-1}$ ); For Pd1, Pd3, and Pd5, all containing a mesityl substituent, the order of activity is Pd5 (55.6  $\times$  10<sup>6</sup> g of PNB  $(mol of Pd)^{-1} h^{-1}) > Pd3 (4.8 \times 10^{6} g of PNB (mol of Pd)^{-1})$  $h^{-1}$ ) > Pd1 (1.9 × 10<sup>6</sup> g of PNB (mol of Pd)<sup>-1</sup>  $h^{-1}$ ). This could be due to the six-membered ring having the looser chelation than that of the five-membered ring, coupled with the coordination of oxygen atom with palladium being weaker than that of nitrogen atom, which were conducive to the rapid coordination and insertion of norbornene monomer. As can be seen from the X-ray structure,  $\pi - \pi$  stacking between the phenyl of the palladacycles and the aryl backbone of the ligands of Pd4 and Pd5 may efficiently remove the steric influence of the substituents in ligands, leaving the palladium center accessible, which leads to the rapid chain initiation.<sup>17</sup> Chain initiation is considered to be the rate-determining step in this system. After activation, the  $\pi - \pi$  stacked arrangement disappears and does not affect the polymerization. Furthermore, as for the same kind of palladacycles, the substituents on nitrogen atom have great influence on the catalytic activity. The Pd(II) complexes substituted by 4-*tert*-butylphenyl showed higher activities than those substituted by mesityl (Pd2 > Pd1, Pd4 > Pd3, Pd6 > Pd5). The presence of a methyl group at the ortho position of mesityl may hinder the coordination and insertion of norbornene,<sup>18</sup> while the presence of a 4-tert-butyl group improves the solubility of the palladacycles to some extent. It is hypothesized that the combination of these effects leads to the order of activities of the catalysts in the current system.

However, its high price and the strict demands for production, transportation, and storage limit the application of MAO. Et<sub>2</sub>AlCl, in contrast, is a common cocatalyst, and the price is much cheaper. Thus, we chose it for comparison. When Et<sub>2</sub>AlCl was used as the cocatalyst, complex Pd6 showed the highest activity of  $29.0 \times 10^6$  g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup> at an Al/Pd ratio of 500 at 40 °C (entry 2, Table 2). Different from the Pd/MAO system, the activities decreased obviously

Table 2. Vinyl Polymerization of Norbornene with Pd1– Pd6 Activated by  $Et_2AlCl^a$ 

entry	cat.	T (°C)	Al/Pd	t (min)	conv. (%)	activity <sup>b</sup>
1	Pd6	20	500	2	24.5	7.4
2	Pd6	40	500	2	96.5	29.0
3	Pd6	60	500	2	70.9	21.3
4	Pd6	80	500	2	29.2	8.8
5	Pd6	40	100	2	94.5	28.4
6 <sup>c</sup>	Pd6	40	100	2	38.5	14.4
7	Pd5	40	100	2	81.7	24.5
8	Pd5	40	100	3	99.8	20.0
9	Pd4	40	100	3	trace	
10	Pd4	60	1500	3	66.4	13.3
11	Pd4	60	1500	5	81.8	9.8
12	Pd3	60	1500	5	12.5	1.5
13	Pd2	60	1500	5	71.0	8.5
14	Pd1	60	1500	5	7.2	0.9

<sup>*a*</sup>Conditions: Pd complexes, 1 µmol; solvent, 1,2-dichlorobenzene;  $V_{\text{total}}$  10 mL; norbornene, 1.0 g; Et<sub>2</sub>AlCl, 2.0 M in hexane. <sup>*b*</sup>Acitivity in units of 10<sup>6</sup> g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup>. <sup>*c*</sup>Pd complexes, 0.8 µmol.

when the temperature was above 60 °C, which would cover the different temperature tolerance of active species produced by different cocatalysts when they interact with metal catalysts. Even if the Al/Pd ratio dropped to 100, the conversion was still over 90% (entry 5, Table 2). Reducing the amount of catalyst to 0.8  $\mu$ mol led to a lower conversion (38.5%) and activity  $(14.4 \times 10^{6} \text{ g of PNB} \text{ (mol of Pd)}^{-1} \text{ h}^{-1}, \text{ entry } 6, \text{ Table 2}).$ Pd5 was then explored under the optimal conditions, with the activity of 24.5×  $10^6$  g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup> and 81.7% conversion. By prolonging the reaction time to 3 min, the conversion was increased to 99.8% accompanied by a slight decrease in activity (20.0× 10<sup>6</sup> g of PNB (mol of Pd)<sup>-1</sup>  $h^{-1}$ , entry 8, Table 2). The C,N-chelated palladacycles showed activities much lower than those of the C,O-chelated palladacycles. Pd4 hardly polymerized norbornene under the same conditions. By adjusting the Al/Pd ratio and the reaction temperature (see the Supporting Information), the yield of PNB was increased to 66.4%. When the reaction time was extended to 5 min, the conversion reached 81.1% (entry 11, Table 2). For the purposes of comparison, the activities of the remaining three palladacycles were investigated under the same conditions (entries 12-14, Table 2). The results showed that the order of activities of the six palladacycles was same as that in Pd/MAO system. As the reaction time was further extended to 10 min, the conversion grew continuously (99.6% for Pd4, 49.5% for Pd3, 97.9% for Pd2, 29.0% for Pd1), proving that these palladacycles have excellent stability (entry 8-11, Table S1). Ethylene polymerization with these complexes was also tested. Unfortunately, no polymer was obtained. Considering the many reported palladium- or nickel-NHC complexes suffering from poor thermal stability and low molecular weight of the obtained polyethylene, the stereo and electronic effects of metal-NHC complexes may require more modification to obtain polyethylene.<sup>7,8a-d,19</sup> Moreover, the size of the metal-chelate ring also plays important roles in determining the properties of transition metal catalysts.<sup>20</sup>

It is difficult to obtain detailed evidence for the mechanism of vinyl polymerization of norbornene catalyzed by palladium catalysts with MAO or  $Et_2AlCl$  as cocatalyst. It is generally accepted that the aluminum cocatalysts capture the ligand to create an empty site for coordination and insertion of olefin.<sup>8c</sup>

The difference in catalytic behaviors between MAO and  $Et_2AlCl$  comes from their different structures and Lewis acidities. MAO is a linear or cyclic oligomer. MAO has a higher Lewis acidity than  $Et_2AlCl$  and leads to faster formation of active metal cation species with empty coordination site to initiate polymerization.<sup>21</sup> In contrast, the polymeric MAO can act as a large weak-coordinated counteranion to make the active metal cation species more free, active, and thermally stable.<sup>22</sup> The Pd/MAO catalytic system showed the highest activity at higher temperature, and its activity is higher than the Pd/Et\_2AlCl system. Also due to the polymeric structure, some aluminum centers in MAO may be shielded. As a result, a larger Al/Pd ratio is needed for the Pd/MAO system.<sup>23</sup>

The PNBs obtained by the Pd/MAO system are insoluble in most organic solvents as in many previous reports,<sup>7,8c,d,15</sup> while those obtained by Pd/Et<sub>2</sub>AlCl systems are slightly soluble in 1,2-dichlorobenzene. Therefore, we only characterized the microstructures of the polymers obtained by Pd/Et<sub>2</sub>AlCl systems by <sup>1</sup>H NMR. The signals appearing in the 0.9-3.0 ppm range and the absence of resonance at 5.0-6.0 ppm in <sup>1</sup>H NMR spectra (Figure S33) indicated that the polymers were vinyl-addition-type products. The missing absorption of a double bond at 1600-1700 cm<sup>-1</sup> in the IR spectra of the polymers (Figures \$34-45) further revealed that the polymerization was not a ROMP type. According to the TGA study (Figure S52), the polymers are thermally stable up to 400  $^{\circ}$ C. The polymers obtained with  $C(sp^2)$ ,N-chelated palladacycles Pd3 and Pd4 displayed glass transition temperatures close to 310 °C as analyzed by means of differential scanning calorimetry (DSC) techniques, while others could not be determined as the glass transition temperature of vinyl polynorbornene is located close to the temperature range where decomposition tends to begin.<sup>24</sup>

#### CONCLUSION

In summary, a series of novel imidazo[1,5-a]pyridinesulfonate-ligated palladacycles were synthesized, and their catalytic behaviors toward norbornene polymerization were studied with MAO or Et<sub>2</sub>AlCl as cocatalyst. The order of activities toward the addition polymerization of norbornene was Pd6 > Pd5 > Pd4 > Pd2 > Pd3 > Pd1. The structure of palladacycles, the type of coordination atom, and the substituent group on the ligands all showed significant influences on the polymerization activities. The Pd1-Pd6/ MAO catalytic system showed high thermal stability and reached the highest activity at 100 °C ( $6.0 \times 10^7$  g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup> with 99.9% conversion). With very low Et<sub>2</sub>AlCl loadings (100 equiv), Pd5 and Pd6 exhibited high activities (up to  $2.9 \times 10^7$  g of PNB (mol of Pd)<sup>-1</sup> h<sup>-1</sup> with 96.5% conversion). Further studies on late-transition-metal complexes based on modified imidazo[1,5-*a*]pyridine-sulfonate ligands and their behaviors toward other  $\alpha$ -olefin (co)polymerization processes are in progress.

#### EXPERIMENTAL SECTION

**General Considerations.** All experiments were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents were distilled from appropriate drying agents under argon before use. Both MAO (1.5 M in toluene, purchased from Beijing InnoChem Co., Ltd.) and  $Et_2AlCl$  (2.0 M in hexane, purchased from J&K Scientific, Ltd.) were used as received. Norbornene (purchased from Alfa Aesar China (Beijing) Chemical Co., Ltd.) and 1,2dichlorobenzene were purified by distillation over calcium hydride. 6-

Ε

Bromopyridine-2-carbaldehyde (1),<sup>25</sup> 2-bromo-6-(dimethoxymethyl) pyridine (2),<sup>25</sup>  $[Pd(OAc)(8-Me-quin-H)]_2$ ,<sup>26</sup>  $[Pd(dmba)(\mu-Cl)]_2$ ,<sup>27</sup> and  $[Pd(o-acetanilido)(\mu-trifluoroacetato)]_2$ <sup>28</sup> were synthesized according to the literature. Other commercially available reagents were purchased and used without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400 spectrometer. HRMS analyses were carried out on Agilent 6520 Q-TOF mass spectrometers. Elemental analyses were performed on a PerkinElmer 240C analyzer. IR spectra were recorded as KBr disks on a Nicolet 380 FT-IR spectrometer. TGA and DSC data were obtained via TA Instrument SDT-2960 and SC-2910 thermal analyzers, respectively.

Isobutyl 6-(Dimethoxymethyl)pyridine-2-sulfonate (3). "BuLi (6.88 mL, 2.5 M in hexane, 17.2 mmol) and "Bu2Mg (17.2 mL, 1.0 M in hexane, 17.2 mmol) were diluted in THF (60 mL). To this stirring mixture, a solution of 2 (10.2 g, 43 mmol) in THF (30 mL) was added dropwise while maintaining the temperature at -5°C. The reaction mixture was stirred at -5 °C for 2 h and added slowly at -78 °C to a THF solution of sulfonyl chloride (5.2 mL, 64.5 mmol). The resulting yellow solution was stirred at -78 °C for 30 min and then allowed to warm to room temperature. Stirring continued overnight, and the solution was cooled to 0 °C. Pyridine (10.4 mL, 129 mmol), 4-dimethylaminopyridine (525 mg, 4.3 mmol), and isobutanol (5.9 mL, 64.5 mmol) were added slowly in order. When the addition was over, the reaction was warmed to room temperature and stirred for 48 h. The volatiles were removed under reduced pressure, and the residue was taken up in ethyl acetate. The mixture was washed with aqueous citric acid solution (15%) and saturated NaCl solution and dried over Na2SO4. The organic solution was evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel, PE/EtOAc = 7:1) to give 3 as a white solid. (4.4 g, 15 mmol, 35%). Mp: 55-57 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.01–7.98 (m, 2H, py-H), 7.82 (dd, J = 6.7, 2.3 Hz, 1H, py-H), 5.37 (s, 1H,  $CH(OCH_3)_2$ ), 4.17 (d, J = 6.5 Hz, 2H,  $CH_2CH(CH_3)_2$ , 3.42 (s, 6H,  $CH(OCH_3)_2$ ), 2.03 (dt, J = 13.4, 6.7Hz, 1H,  $CH_2CH(CH_3)_2$ ), 0.91 (d, J = 6.7 Hz, 6H,  $CH_2CH(CH_3)_2$ ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.8, 153.8, 138.7, 124.9, 122.7, 103.8, 78.9, 54.3, 28.2, 18.5. HRMS (ESI, m/z): calcd for  $C_{12}H_{19}NO_5S [M + H]^+$  290.1062. Found 290.1059.

Isobutyl 6-Formylpyridine-2-sulfonate (4). A flask was charged with 3 (4.4 g, 15 mmol) and p-toluenesulfonic acid (336.0 mg, cat.). Acetone (60 mL) and water (9 mL) were added via syringe. The reaction was refluxed at 90 °C for 6 h. The mixture was cooled to room temperature, and most of the solvent was removed. The mixture was alkalized by the addition of saturated NaHCO<sub>3</sub> aqueous solution and extracted three times with dichloromethane  $(3 \times 100 \text{ mL})$ . The extracts were combined, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The crude sulfonate was purified using column chromatography (silica gel, PE/EtOAc = 5:1), yielding 2.95 g (12 mmol, 81%) of sulfonate product 4 as white solid. Mp: 30-32 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.10 (s, 1H, CHO), 8.26–8.16 (m, 3H, py-H), 4.21  $(d, J = 6.5 Hz, 2H, CH_2CH(CH_3)_2), 2.04 (dt, J = 13.3, 6.6 Hz, 1H,$  $CH_2CH(CH_3)_2$ , 0.94 (d, J = 6.7 Hz, 6H,  $CH_2CH(CH_3)_2$ ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 191.3, 155.3, 152.7, 139.7, 126.8, 124.6, 79.2, 28.3, 18.5. HRMS (ESI, m/z): calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>4</sub>S [M + H]<sup>+</sup> 244.0644. Found 244.0633.

**Ligand L1.** A solution of 4 (1.2 g, 5 mmol), 2,4,6-trimethylaniline (676 mg, 5 mmol), and *p*-toluenesulfonic acid (86 mg, 0.5 mmol) in toluene (20 mL) was stirred at 120 °C for 8 h. The suspension was cooled to room temperature before it was added to a solution of paraformaldehyde (187.6 mg, 6.25 mmol) in toluene (20 mL). HCl (1.25 mL, 4 M in dioxane) was added. The resulting brown solution was stirred at 70 °C for 12 h. Upon cooling to room temperature, the mixture was separated. After removal of solvents, the residue was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 40:1) to give L1 as a white solid. (1.33 g, 4.2 mmol, 84%). Mp: >300 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): $\delta$  9.72 (s, 1H, NCHN), 7.85 (d, *J* = 6.8 Hz, 1H, py-H), 7.71 (d, *J* = 9.2 Hz, 1H, py-H), 7.60 (s, 1H, im-H)), 7.43 (dd, *J* = 6.8, 8.8 Hz, 1H, py-H), 7.08 (s, 2H, Ar–H)), 2.40 (s, 3H, Ar–CH<sub>3</sub>), 2.04 (s, 6H, Ar–CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): 140.3, 138.3, 133.9, 131.6, 130.4, 129.2, 127.0, 125.1,

119.4, 116.0, 115.8, 20.6, 16.8. HRMS (ESI, m/z): calcd for  $C_{16}H_{16}N_2O_3S$  [M + H]<sup>+</sup> 317.0960. Found 317.0958.

**Ligand L2.** The same procedure as that described for the synthesis of **L1** was used. Reaction of 4 (1.2 g, 5 mmol), 4-*tert*-butyl benzenamine (746 mg, 5 mmol), and *p*-toluenesulfonic acid (86 mg, 0.5 mmol) gave **L2** (972 mg, 64%) as a white solid. Mp: >300 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.80 (s, 1H, NCHN), 8.85 (s, 1H, im-*H*), 8.00 (d, *J* = 9.2 Hz, 1H, py-*H*), 7.83 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.71 (d, *J* = 8.6 Hz, 2H, Ar-*H*), 7.55 (d, *J* = 6.9 Hz, 1H, py-*H*), 7.42 (dd, *J* = 9.2, 7.0 Hz, 1H, py-*H*), 1.35 (s, 9H, Ar-C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): 153.4, 138.2, 132.5, 130.4, 126.9, 125.0, 124.2, 123.1, 119.2, 115.8, 113.9, 34.6, 30.8. HRMS (ESI, *m*/*z*): calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S [M + H]<sup>+</sup> 331.1116. Found 331.1117.

Complex Pd1. A mixture of L1 (316 mg, 1.0 mmol),  $[Pd(OAc)(8-Me-quin-H)]_2$  (0.308 g, 0.5 mmol), and 6 equiv of potassium carbonate (829 mg, 6 mmol) was placed in a roundbottomed flask and dissolved in 20 mL of acetonitrile. The reaction mixture was stirred under reflux for 24 h and then cooled to room temperature. After removal of solvent under reduced pressure, the residue was dissolved in CH2Cl2 and purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/EtOAc = 10:1) to give Pd1 as a white solid (293 mg, 52%). Mp: 250 °C (dec.). Anal. Calcd for C<sub>26</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>PdS: C, 55.37; H, 4.11; N, 7.45. Found: C, 55.51; H, 4.30; N, 7.27. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.08 (d, J = 4.5 Hz, 1H, py-H), 8.22 (d, I = 8.2 Hz, 1H, Ar-H), 7.61 (d, I = 6.6 Hz, 1H, Ar-H, 7.52–7.44 (m, 3H, Ar-H), 7.34 (t, J = 7.6 Hz, 1H, Ar-H), 7.26 (s, 1H, im-H), 7.12 (d, J = 7.0 Hz, 1H, py-H), 7.04 (s, 2H, Ar-H), 6.96 (dd, J = 9.0, 6.9 Hz, 1H, py-H), 2.57 (s, 2H, Ar-CH<sub>2</sub>-Pd), 2.40 (s, 3H, Ar– $CH_3$ ), 2.16 (s, 6H, Ar– $CH_3$ ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 158.0, 150.7, 149.2, 148.3, 140.2, 139.7, 137.6, 136.7, 134.9, 132.5, 129.1, 128.5, 128.1, 127.6, 123.1, 122.5, 121.4, 119.7, 115.9, 114.4, 21.1, 18.2, 16.9. HRMS (ESI, m/z): calcd for C<sub>26</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>PdS [M + H]<sup>+</sup> 564.0573. Found 564.0570.

Complex Pd2. The same procedure as that described for the synthesis of Pd1 was used. L2 (330 mg, 1.0 mmol), [Pd(OAc)(8-Mequin-H)]<sub>2</sub> (0.308 g, 0.5 mmol), and potassium carbonate (829 mg, 6 mmol) were used to give Pd2 (353 mg, 61%) as a white solid. Mp: 240 °C (dec.). Anal. Calcd for C<sub>27</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>PdS: C, 56.11; H, 4.36; N, 7.27. Found: C, 56.18; H, 4.33; N, 7.35. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ :  $\delta$  9.08 (dd, I = 1.6, 4.8 Hz, 1H, py-H), 8.23 (dd, I = 1.6, 8.4Hz, 1H, Ar-H), 7.65-7.63 (m, 2H, Ar-H), 7.61 (dd, J = 1.2, 6.8 Hz, 1H, Ar-H), 7.55 (d, J = 3.6 Hz, 2H, Ar-H), 7.53 (t, J = 2.0 Hz, 1H, py-*H*), 7.50–7.47 (m, 2H, Ar–*H*), 7.44 (dd, *J* = 1.2, 9.2 Hz, 1H, Ar– *H*), 7.31 (t, *J* = 7.2, 1H, Ar–*H*), 7.01 (dd, *J* = 0.8, 6.8 Hz, 1H, py-*H*), 6.97 (dd, J = 6.8, 9.2 Hz, 1H, im-H), 2.57 (s, 2H, Ar-CH<sub>2</sub>-Pd), 1.39 (s, 9H, Ar-C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 157.4, 153.0, 150.7, 149.4, 148.4, 140.3, 138.1, 137.6, 132.5, 128.6, 127.7, 127.5, 126.6, 126.0, 123.1, 122.8, 121.6, 119.5, 116.0, 114.6, 34.9, 31.3, 19.8. HRMS (ESI, m/z): calcd for C<sub>27</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>PdS [M + H]<sup>+</sup> 578.0730. Found 578.0728.

**Complex Pd3.** The same procedure as that described for the synthesis of **Pd1** was used. **L1** (316 mg, 1.0 mmol),  $[Pd(dmba)(\mu-Cl)]_2$  (307.5 mg, 0.5 mmol), and potassium carbonate (829 mg, 6 mmol) were used to give **Pd3** (476 mg, 0.86 mmol, 86%) as a white solid. Mp: 200 °C (dec.). Anal. Calcd for  $C_{25}H_{27}N_3O_3PdS$ : C, 54.01; H, 4.89; N, 7.56. Found: C, 53.97; H, 5.00; N, 7.47. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.55 (d, J = 9.2 Hz, 1H, py-H), 7.45 (d, J = 9.2 Hz, 1H, py-H), 7.32 (s, 1H, im-H), 6.96 (dd, J = 9.0, 6.9 Hz, 1H, Ar–H), 6.63–6.62 (m, 4H, Ar–H), 6.50 (d, J = 7.4 Hz, 1H, Ar–H), 6.43–6.39 (m, 1H, py-H), 3.72 (s, 2H, Ar–CH<sub>2</sub>-N), 2.63 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.36 (s, 6H, Ar–CH<sub>3</sub>), 2.05 (s, 3H, Ar–CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 161.1, 146.0, 144.8, 140.1, 138.4, 137.7, 136.3, 133.7, 131.4, 128.9, 123.7, 122.8, 122.5, 121.3, 119.6, 116.1, 114.9, 71.4, 49.1, 20.6, 19.8. HRMS (ESI, *m/z*): calcd for  $C_{25}H_{27}N_3O_3PdS$  [M + H]<sup>+</sup> 556.0886. Found 556.0886.

**Complex Pd4.** The same procedure as that described for the synthesis of **Pd1** was used. **L2** (330 mg, 1.0 mmol),  $[Pd(dmba)(\mu-Cl)]_2$  (307.5 mg, 0.5 mmol), and potassium carbonate (829 mg, 6 mmol) were used to give **Pd4** (568 mg, 1.0 mmol, >99%) as a white solid. Mp: 185 °C. Anal. Calcd for  $C_{26}H_{29}N_3O_3PdS$ : *C*, 54.78; H,

5.13; N, 7.37. Found: C, 55.03; H, 4.89; N, 6.99. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.73 (d, J = 8.4 Hz, 2H, Ar–H), 7.65 (s, 1H, im-H), 7.57 (d, J = 6.8 Hz, 1H, py-H), 7.45 (d, J = 9.6 Hz, 1H, py-H), 7.13 (d, J = 8.0 Hz, 2H, Ar–H), 6.99 (dd, J = 7.6, 8.8 Hz, 1H, Ar–H), 6.62 (d, J = 7.6 Hz, 1H, Ar–H), 6.53 (t, J = 7.2 Hz, 1H, py-H), 6.23 (t, J = 7.6 Hz, 1H, Ar–H), 6.13 (d, J = 7.6 Hz, 1H, Ar–H), 6.23 (t, J = 7.6 Hz, 1H, Ar–H), 6.13 (d, J = 7.6 Hz, 1H, Ar–H), 2.71 (br, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.51 (s, 1H, Ar–CH<sub>2</sub>-N), 1.40 (s, 1H, Ar–CH<sub>2</sub>-N), 1.13 (s, 9H, Ar–C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 158.4, 151.8, 145.5, 145.3, 140.3, 137.7, 137.2, 132.4, 125.8, 124.9, 124.5, 122.9, 122.8, 121.0, 119.5, 116.1, 113.4, 71.3, 34.4, 31.0. HRMS (ESI, m/z): calcd for C<sub>26</sub>H<sub>29</sub>N<sub>3</sub>O<sub>3</sub>PdS [M + H]<sup>+</sup> 570.1043. Found 570.1034.

Complex Pd5. The same procedure as that described for the synthesis of Pd1 was used. L1 (316 mg, 1.0 mmol), [Pd(oacetanilido)( $\mu$ -trifluoroacetato)]<sub>2</sub> (354 mg, 0.5 mmol), and potassium carbonate (829 mg, 6 mmol) were used to give Pd5 (253 mg, 43%) as a pale yellow solid. Mp: 236 °C (dec.). Anal. Calcd for C24H23N3O4PdS: C, 51.85; H, 4.17; N, 7.56. Found: C, 51.68; H, 3.96; N, 7.41. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  11.00 (s, 1H, N-H), 8.07 (s, 1H, im-H), 7.72 (d, J = 8.8 Hz, 1H, py-H), 7.35 (d, J =6.8 Hz, 1H, py-H), 7.11 (dd, J = 6.8, 9.2 Hz, 1H, Ar-H), 6.72 (t, J = 7.2 Hz, 1H, Ar-H), 6.65 (d, J = 7.2 Hz, 1H, Ar-H), 6.60 (s, 2H, Ar-H), 6.54 (d, J = 7.2 Hz, 1H, Ar-H), 6.47 (t, J = 7.2 Hz, 1H, py-H), 2.22 (s, 3H, CO-CH<sub>3</sub>), 2.18 (s, 6H, Ar-CH<sub>3</sub>), 2.05 (s, 3H, Ar-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  169.37, 154.85, 140.87, 139.92, 137.87, 136.35, 133.63, 133.46, 131.42, 128.90, 127.47, 124.35, 123.09, 122.55, 121.25, 117.35, 116.11, 115.58, 21.87, 20.77, 19.74. HRMS (ESI, m/z): calcd for  $C_{24}H_{23}N_3O_4PdS$  [M + H]<sup>+</sup> 556.0522. Found 556.0518.

**Complex Pd6.** The same procedure as that described for the synthesis of **Pd1** was used. **L2** (330 mg, 1.0 mmol),  $[Pd(o-acetanilido)(\mu-trifluoroacetato)]_2 (354 mg, 0.5 mmol), and potassium carbonate (829 mg, 6 mmol) were used to give$ **Pd6** $(148 mg, 26%) as a pale yellow solid. Mp: 238 °C (dec.). Anal. Calcd for C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>PdS: C, 52.68; H, 4.42; N, 7.37. Found: C, 52.43; H, 4.65; N, 7.09. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) <math>\delta$  9.70 (s, 1H, N–H), 7.65 (s, 1H, im-H), 7.53–7.49 (m, 4H, Ar–H), 7.08 (d, *J* = 8.4 Hz, 2H, Ar–H), 6.96 (dd, *J* = 7.2, 8.8 Hz, 1H, py-H), 6.59 (d, *J* = 8.0 Hz, 1H, Ar–H), 6.12 (t, *J* = 7.2 Hz, 1H, Ar–H), 6.25 (d, *J* = 7.6 Hz, 1H, py-H), 6.12 (t, *J* = 7.2 Hz, 1H, py-H), 2.05 (s, 3H, CO–CH<sub>3</sub>), 1.12 (s, 9H, Ar–C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.94, 154.86, 151.59, 140.17, 139.97, 137.47, 132.38, 132.33, 126.51, 125.89, 125.15, 124.34, 123.49, 122.54, 119.99, 116.57, 116.05, 114.21, 34.47, 30.99, 22.00. HRMS (ESI, *m/z*): calcd for C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>PdS [M + H]<sup>+</sup> 570.0679. Found 570.0674.

**Crystallographic Studies.** Single crystals of **Pd1**, **Pd2**, **Pd4**, and **Pd5** suitable for X-ray diffraction were obtained from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Data collections were carried out on a Rigaku Saturn 724 CCD diffractometer equipped with a rotating anode system at 113(2) K by using graphite-monochromated Mo K $\alpha$  radiation ( $\omega$ -2 $\theta$  scans,  $\lambda$  = 0.71073 Å). Semi-empirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined using the full-matrix least-squares method. Calculations were performed by using the SHELXL-97 program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. The molecular structures of complexes Pd1, Pd2, and Pd4 contain one CH<sub>2</sub>Cl<sub>2</sub> molecule of solvation, respectively.

**Norbornene Polymerization.** In a typical procedure, 1.00 g of norbornene in 5.0 mL of 1,2-dichlorobenzene and an exact amount of MAO or  $Et_2AlCl$  solution were added into a flask (100 mL) with stirring under an Ar atmosphere. After the mixture was kept at the desired temperature for 3 min, the right amount of the palladium complex dissolved in dichlorobenzene was injected into the flask with a syringe, and the reaction was started. After the desired time, the polymerization was terminated by the addition of 10% HCl in ethanol. The precipitated polymer was washed with ethanol and water and dried at 60 °C in vacuo to a constant weight. For all the polymerization procedures, the total reaction volume was 10 mL, which can be achieved by the variation of the amount of added dichlorobenzene when necessary.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.9b00495.

Polymerization tables, NMR spectra for 1–4, NMR and IR spectra for L1–L2 and Pd1–Pd6; NMR and IR spectra, DSC, and TGA spectra of the PNB obtained (PDF)

#### Accession Codes

CCDC 1899681, 1899685, 1899686, and 1907389 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data\_request/cif, or by emailing data\_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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