

# Synthesis, Structures, and Norbornene ROMP Behavior of *o*-Aryloxide-N-Heterocyclic Carbene *p*-Cymene Ruthenium Complexes

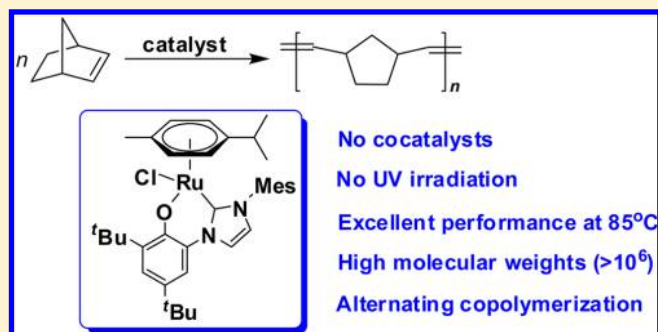
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## Supporting Information

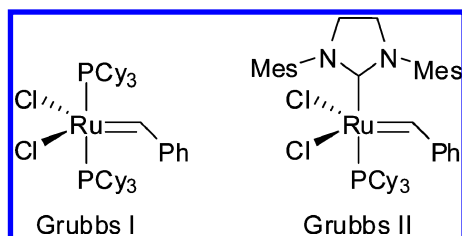
**ABSTRACT:** Treatment of the *o*-hydroxyaryl imidazolium proligands (2-OH-3,5-<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)(R)(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sup>+</sup>Br<sup>-</sup> (R = <sup>t</sup>Pr (1a), <sup>t</sup>Bu (1b), Ph (1c), Mes (1d)) with 3 equiv of Ag<sub>2</sub>O afforded the corresponding silver complexes 2a–d. The subsequent metal-exchange reactions with [(*p*-cymene)-RuCl<sub>2</sub>]<sub>2</sub> at room temperature yielded the desired *o*-aryloxide-N-heterocyclic carbene *p*-cymene ruthenium complexes 3a–d in nearly quantitative yields. All the complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, high-resolution mass spectrometry (HRMS), and elemental analysis. The molecular structure of complex 3b was determined by single-crystal X-ray diffraction analysis. The ring-opening metathesis polymerization (ROMP) of norbornene (NBE) with 3a–d was studied. Among them, complex 3d showed high activity and efficiency toward ROMP of NBE at 85 °C without the need for any cocatalyst, and polymers with very high molecular weight (>10<sup>6</sup>) and narrow molecular weight distributions were obtained. This complex can also catalyze the alternating copolymerization of NBE and cyclooctene (COE).



## INTRODUCTION

The discovery of the ruthenium benzylidene catalyst (Grubbs I, Chart 1) by Grubbs and co-workers in the mid-1990s<sup>1</sup> was a

Chart 1



solid milestone in the transformation of olefin metathesis to a versatile and powerful tool for the construction of a variety of small molecules and macromolecules. Later the introduction of a N-heterocyclic carbene (NHC) ligand into Grubbs I led to the development of the second-generation Grubbs catalyst (Grubbs II, Chart 1),<sup>2</sup> which generally gives rise to higher activities, increased thermal stability, and high tolerance to broad functional groups. A large number of well-defined Ru benzylidene catalysts have been subsequently developed.<sup>3</sup>

In comparison to the well-defined ruthenium catalysts featuring a ruthenium–carbon double bond, the ill-defined ones do not contain an alkylidene fragment in their molecules.

In these catalyst systems the active alkylidenes are generally formed in situ by the addition of a carbene source or by coordination of the substrate to the coordinatively unsaturated complex and a subsequent 1,2-H shift. The ill-defined ruthenium catalysts are generally readily commercially available or are easily prepared from commercially available compounds and sometimes exhibit performance comparable to or even better than that of the well-defined catalysts and allow for straightforward synthetic procedures.<sup>4</sup> After the first highly efficient arene ruthenium ring-opening metathesis polymerization (ROMP) catalyst (*p*-cymene)RuCl<sub>2</sub>(PCy<sub>3</sub>) was pioneered by the Noels group in 1992,<sup>5</sup> *p*-cymene-based catalytic systems involving different types of ligands such as phosphine ligands,<sup>6,7</sup> bidentate Schiff base ligands,<sup>8,9</sup> and NHC ligands<sup>10,11</sup> have been extensively investigated by different groups.

Recently, a great deal of research effort has been made toward the study of transition-metal complexes with anion-tethered NHC ligands.<sup>12</sup> As an anchor, the introduced anion groups can reduce the tendency of ligand dissociation, via enhancing the bond between the NHCs and metal centers. In our previous work we developed the *o*-hydroxyaryl imidazolium proligands and synthesized a series of *o*-aryloxide-N-heterocyclic carbene palladium and nickel complexes, which showed

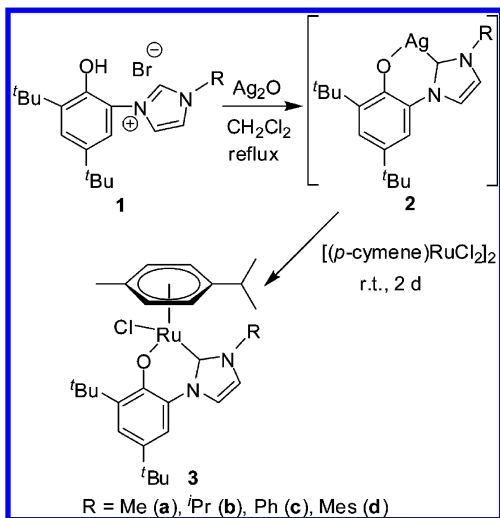
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high activities for the addition polymerization of norbornene (NBE) in the presence of MAO.<sup>13</sup> As a part of the systematic study of metal complexes bearing *o*-aryloxide-N-heterocyclic carbene ligands, in this work, we report the synthesis and structures of a series of *o*-aryloxide-N-heterocyclic carbene *p*-cymene ruthenium complexes. The ROMP of NBE with these complexes was also studied. It is interesting to note that one of the complexes exhibits almost the same high activity and efficiency toward ROMP of NBE at 85 °C as Grubbs I, without the need for any cocatalyst, whereas the resultant polymer has a much higher molecular weight (>10<sup>6</sup>) than that generated using Grubbs I. This catalyst is also effective at catalyzing the copolymerization of NBE and cyclooctene (COE), producing alternating copolymers possessing high molecular weights and narrow molecular weight distributions.

## RESULTS AND DISCUSSION

**Synthesis of *o*-Aryloxide-N-Heterocyclic Carbene *p*-Cymene Ruthenium Complexes.** The synthesis of **3**, derived from the proligands **1**, is slightly different from the well-established approach to other transition-metal complexes in our laboratory.<sup>15</sup> Treatment of **1a–d** with 3 equiv of Ag<sub>2</sub>O afforded the corresponding silver complexes **2a–d**. The subsequent metal-exchange reactions with [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> at room temperature yielded the desired *o*-aryloxide-N-heterocyclic carbene *p*-cymene ruthenium complexes **3a–d** in nearly quantitative yields (Scheme 1).

Scheme 1



Complexes **2a–d** and **3a–d** are all air and moisture stable. In their <sup>1</sup>H NMR spectra, the signals of the phenol proton and the imidazole proton at the C-2 position, appearing for compound **1**, completely disappear. The characteristic signals of the carbene carbons in their <sup>13</sup>C NMR spectra (161.8 (**2a**), 161.6 (**2b**), 161.7 (**2c**), 161.6 (**2d**); 174.5 (**3a**), 174.0 (**3b**), and 173.0 ppm (**3d**)) are comparable to those of the previously reported silver and ruthenium NHC complexes.<sup>14,15</sup>

We could easily grow single crystals of **3b** from a CH<sub>2</sub>Cl<sub>2</sub>/ether solution. The molecular structure of **3b** was confirmed by single-crystal X-ray diffraction analysis (Figure 1). Its molecule consists of an η<sup>6</sup>-bonding *p*-cymene ligand, an anionic chloride, and a bidentate *o*-aryloxide-NHC ligand. The ligand retains the characteristic bond angle for a singlet carbene (104.87(16)° for

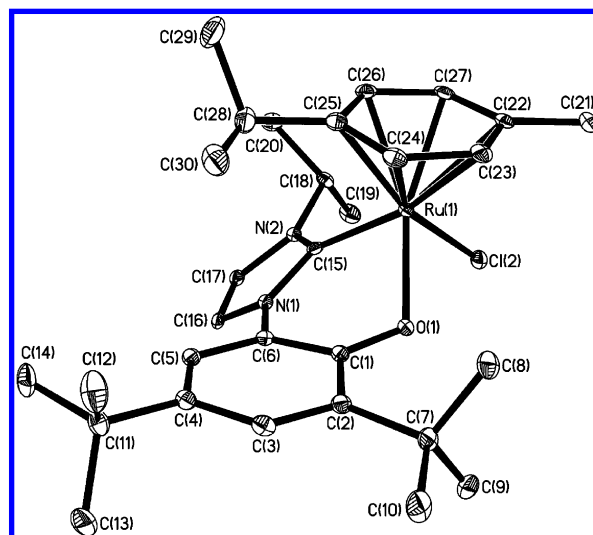


Figure 1. ORTEP diagram of **3b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

the imidazolydene). The Ru–C(carbene) (2.022(2) Å) and Ru–O (2.0964(12) Å) bond lengths are analogous to those in the *o*-aryloxide-NHC ligated Ru complexes.<sup>10</sup> The Ru–Cl, Ru–centroid (arene), and average Ru–C (arene) bond lengths are 2.4069(9), 1.697, and 2.2088 Å, respectively. The angles C(15)–Ru(1)–O(1), C(15)–Ru(1)–Cl(2), C(15)–Ru(1)–centroid (arene), O(1)–Ru(1)–centroid (arene), and Cl(2)–Ru(1)–centroid (arene) are 81.43(6), 86.74(6), 130.42, 130.38, and 127.02°, respectively. The isopropyl group on the arene ligand is slightly distorted away from the metal center as a result of steric repulsion, analogous to the previously reported results.<sup>11</sup>

**Norbornene Polymerization.** ROMP has become a powerful methodology for the synthesis of linear or branched polymers with narrow molecular weight distributions.<sup>3a</sup> We have tested the catalytic activity of complexes **3a–d** toward ROMP of NBE at 85 °C with and without the presence of TMSD, and the polymerization results are summarized in Table 1. **3a,b** both showed moderate activity with and without TMSD

Table 1. ROMP of NBE with Ruthenium Catalysts with and without the Presence of TMSD<sup>a</sup>

entry	cat.	<i>t</i>	yield (%)	<i>M<sub>n</sub></i> (×10 <sup>3</sup> )	PDI	cis (%)
1	<b>3a</b>	3 h	29	902	2.02	39
2	<b>3a</b> + TMSD	3 h	29	98	3.59	42
3	<b>3b</b>	3 h	43	1314	1.97	40
4	<b>3b</b> + TMSD	3 h	47	276	3.21	45
5	<b>3c</b>	3 h	trace			
6	<b>3c</b> + TMSD	3 h	30	25	5.26	64
7	<b>3d</b>	3 min	80 <sup>b</sup>	1522	1.95	42
8	<b>3d</b>	1 h	>99 <sup>c</sup>	1202	1.96	43
9	<b>3d</b> + TMSD	1 h	86	294	1.96	44
10	[( <i>p</i> -cymene)RuCl <sub>2</sub> ] <sub>2</sub>	3 h	trace			
11	[( <i>p</i> -cymene)RuCl <sub>2</sub> ] <sub>2</sub> + TMSD	3 h	40	53	6.11	45
12	Grubbs I	3 min	99	217	1.93	11

<sup>a</sup>General polymerization conditions: 30 mL of toluene; 1.0 g (10.62 mmol) of NBE; [cat.] = 0.167 mmol L<sup>-1</sup>; 85 °C; GPC versus polystyrene standards. <sup>b</sup>The reaction mixture quickly turned into a gel-like substance. <sup>c</sup>0.378 g (4.0 mmol) of NBE, [NBE]/[cat.] = 800.

(entries 1–4). In contrast, **3c** itself exhibited no activity (entry 5), while the addition of TMSD to the reaction mixture gave a moderate yield (entry 6). It is clear that the polymers obtained in the presence of TMSD have much lower molecular weights and higher PDIs. Much to our surprise, the mesityl complex **3d** exhibited quickly increasing activity at elevated temperatures and remarkably high activity was achieved at 85 °C (Table 2).

**Table 2. ROMP of NBE with **3d** at Different Temperatures<sup>a</sup>**

entry	cat.	T (°C)	t	conversion (%)	M <sub>n</sub> (×10 <sup>3</sup> )	PDI	cis (%)
1	<b>3d</b>	25	3 h	16.3	1543	2.02	0.42
2 <sup>b</sup>	<b>3d</b>	45	50 min	62.8	1607	1.84	0.42
3 <sup>b</sup>	<b>3d</b>	65	12 min	70.6	1765	1.90	0.42
4 <sup>b</sup>	<b>3d</b>	85	3 min	80.0	1522	1.95	0.42

<sup>a</sup>Polymerization conditions: 30 mL of toluene; norbornene 1.0 g; [cat.] = 5 μmol. <sup>b</sup>The reaction mixture turned into a gel-like substance; the yield increased (nearly 100%) with a longer reaction time.

Gelation of the reaction mixture occurred within 3 min at 85 °C, and a polymer with a high molecular weight (>10<sup>6</sup>) was obtained in 80% yield (entry 7). A quantitative yield was obtained upon reducing the concentration of NBE (entry 8). These catalytic systems worked well even in the dark, indicating that the formation of the active species does not require light irradiation.

Complex **3d** exhibited high activity and efficiency almost identical with those of Grubbs I under the same conditions, but the polymers obtained using **3d** have much higher molecular weights than that obtained using Grubbs I (Table 1, entries 7, 8, and 12). Since **3a–d** are stable 18-electron complexes, the formation of the active species might follow the same mechanism that has been widely accepted for the *p*-cymene ruthenium system.<sup>3e,8a,9</sup> The release of a *p*-cymene ligand from **3**, followed by the coordination of NBE and a subsequent 2,3-hydrogen shift, generates an active ruthenium carbene species which propagates the ROMP in the same way as the well-defined ruthenium catalysts do (Scheme 2).

It should be noted that the *p*-cymene ruthenium complex incorporating a bidentate *o*-aryloxy-substituted saturated

NHC ligand exhibited very low efficiency toward ROMP of NBE, even in the presence of cocatalysts such as trimethylsilyldiazomethane (TMSD) and phenylacetylene.<sup>11</sup> In general, the ruthenium catalysts with saturated NHC are far more reactive than the corresponding unsaturated NHC-derived catalysts.<sup>10d,16</sup> Thus, the reasons for the high activity of **3d** are still unclear. The steric effect of the bulky *tert*-butyl group at the ortho position of the aryloxy may be helpful for increasing the activity.

**NBE and COE Copolymerization.** We next turned our attention to the homopolymerization of other olefins. Different from the case for most Noels-type<sup>4–11</sup> and all Grubbs-type initiators,<sup>1–4</sup> complexes **3a–d** were inactive toward ROMP of COE, even in the presence of TMSD, indicating that the active ruthenium carbene species cannot be formed from **3** and COE (Table 3, entry 2). This interesting behavior allowed us to study the copolymerization of NBE and COE. A great deal of research effort has been recently devoted to the synthesis and study of alternating copolymers by the metathesis copolymerization of two different monomers.<sup>17</sup>

To explore the copolymerization potential of complex **3d**, various ratios of NBE and COE were used for copolymerization (Table 3). As shown in Table 3, the percentage of the alternating diads poly(NBE-*alt*-COE) in the obtained copolymers ( $2.7 \times 10^5 < M_w < 12 \times 10^5$ ,  $1.4 < \text{PDI} < 2.1$ ) gradually increases as the NBE/COE ratio decreases. GPC investigations showed a single, smooth, monomodal peak (see the Supporting Information), indicating that the polymer is not a physical mixture of the homopolymers of NBE and COE. The <sup>13</sup>C NMR spectra of the copolymers derived from various ratios of NBE and COE further support the alternate incorporation of the two monomers in the ROMP. A representative <sup>13</sup>C NMR spectrum of a copolymer is shown in Figure 2. The signals for the alternating diads were observed around δ 134.2–134.6 and 128.1 ppm on the basis of the literature data.<sup>17d–h,j</sup> The signals for the poly(COE) block were also detected at δ 129.4 and 129.8 ppm. The signals around δ 132–134 ppm were assigned to the poly(NBE) block. Not all ruthenium metathesis catalysts are suitable for the catalytic synthesis of alternating copolymers. It was reported that the copolymerization of a 1/1 NBE/COE mixture using Grubbs I catalyst afforded a copolymer consisting of a poly(NBE) block and a poly(COE) block.<sup>17d,e</sup>

Controlling the composition of polymers is a very important issue, since polymers with different compositions often exhibit different properties. For the alternating copolymers produced by ROMP using complex **3d**, the percentages of the alternating diads were roughly controlled from 0% to 53% by changing the relative ratios of the two monomers.

## CONCLUSION

In summary, we have successfully developed a series of *o*-aryloxy-NHC ligated Ru arene complexes which can be used as single-component catalysts to initiate the ROMP of NBE. What is remarkable is that complex **3d** exhibits very high activity and efficiency toward the ROMP of NBE at 85 °C. The catalytic performance for **3d** is comparable to that for Grubbs I, but the generated polymers have much higher molecular weights (>10<sup>6</sup>). Complex **3d** was also found to efficiently catalyze the copolymerization of NBE and COE, generating the alternating copolymers with high molecular weights and narrow molecular weight distributions. The degree of alternation can be controlled by changing the relative stoichiometry of NBE

**Scheme 2**

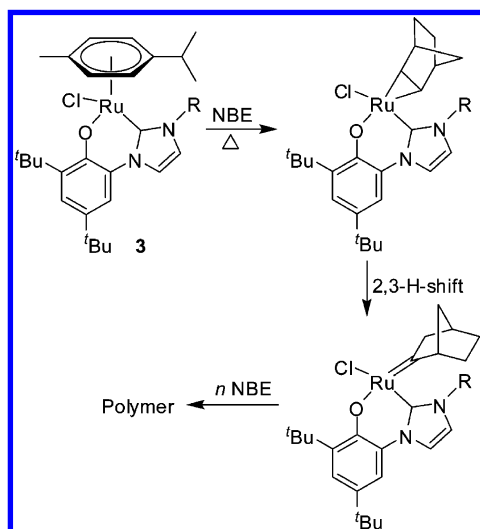
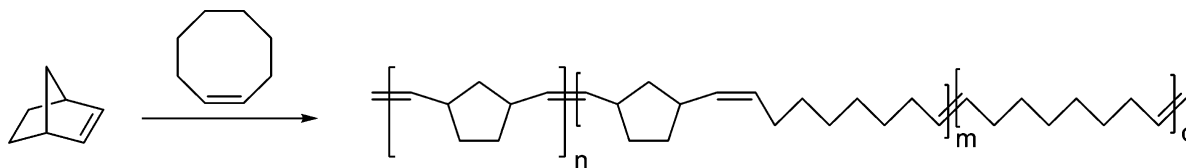
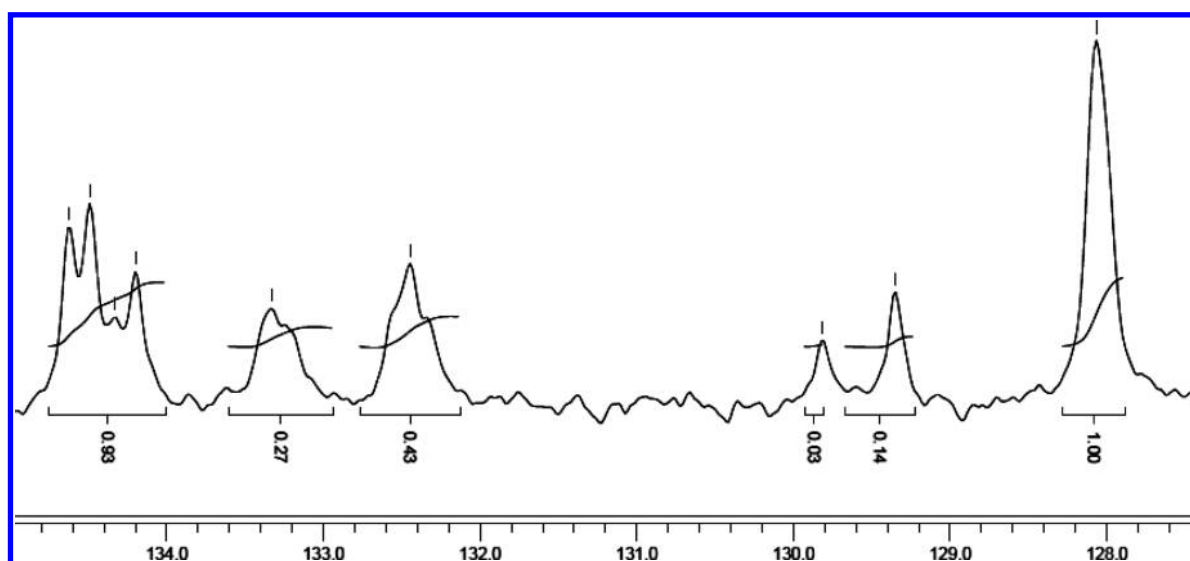


Table 3. Alternating Copolymerization of NBE and COE using the Initiator 3d<sup>a</sup>

entry	cat./NBE/COE	<i>t</i> (h)	<i>M<sub>n</sub></i> (×10 <sup>-3</sup> )	PDI	poly(NBE) (%) <sup>b</sup>	poly(NBE- <i>alt</i> -COE) (%) <sup>b</sup>	poly(COE) (%) <sup>b</sup>
1 <sup>c</sup>	1/800/0	1	1202	1.96	100	0	0
2	1/0/1000	24					
3	1/800/200	2	1164	2.05	97	3	0
4	1/500/500	12	377	1.50	82	18	0
5	1/500/1000	12	347	1.61	68	32	0
6	1/500/1500	12	379	1.52	64	34	2
7	1/500/2000	12	330	1.67	44	42	14
8	1/500/3000	12	383	1.46	33	49	18
9	1/500/4000	12	351	1.53	35	51	14
10	1/500/5000	12	269	1.71	38	53	9

<sup>a</sup>Polymerization conditions: 10 mL of toluene; [cat.] = 0.5 mmol L<sup>-1</sup>; 85 °C; GPC versus polystyrene standards. <sup>b</sup>Calculated from the <sup>13</sup>C NMR spectra. <sup>c</sup>Polymerization conditions: 30 mL of toluene (also see Table 1, entry 8).

Figure 2. <sup>13</sup>C NMR spectrum of a copolymer obtained via the copolymerization of NBE and COE triggered by 3d (Table 3, entry 10).

and COE. Further investigations into the alternating copolymerization of other olefins are still in progress.

## EXPERIMENTAL SECTION

**General Considerations.** All experimental manipulations 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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400, Bruker AV300, or Varian 300 spectrometer, while ESI mass spectra and HRMS measurements were carried out on Thermo Finnigan LCQ Advantage and Varian 7.0 T FTICR mass spectrometers, respectively. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The molecular weights and molecular weight distribution were obtained on Polymer Laboratories PL-GPC 50 and GPC (Waters 510 liquid chromatograph connected with four styragel GPC columns (guard, 10<sup>3</sup> Å, 10<sup>4</sup> Å, 10<sup>5</sup> Å), and a Waters 410 differential refractometer. All of the *o*-aryloxide-NHC prolignands were prepared according to the literature procedures.<sup>13</sup>

**General Procedures for Preparation of the *o*-Aryloxide-NHC Ligated Silver Complexes 2a–d.** The *o*-hydroxyaryl imidazolium prolignands (2-OH-3,5-<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>2</sub>)(R)(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sup>+</sup> Br<sup>-</sup> (R = Me (1a), <sup>i</sup>Pr (1b), Ph (1c), Mes (1d); 1.0 mmol) and Ag<sub>2</sub>O (0.696 g, 3 mmol)

were added to a round-bottom flask equipped with a cooler. Dried CH<sub>2</sub>Cl<sub>2</sub> (20.0 mL) was added to the flask. The reaction mixture was stirred at reflux for 4 h, cooled to room temperature, and diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The mixture was then filtered through a pad of Celite (2/5 cm, w/1), that successively was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL). The solvent was removed under reduced pressure to provide the silver complex as a yellow solid in a yield of ~99% (based on the prolignands 1a–d).

**Compound 2a (R = Me).** Yield: 99%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.22 (d, 1H, *J* = 2.51 Hz, *im-H*), 7.07 (s, 1H, *Ar-H*), 7.03 (s, 1H, *Ar-H*), 6.77 (d, 1H, *J* = 2.37 Hz, *im-H*), 3.76 (s, 3H, NCH<sub>3</sub>), 1.25 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.24 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.8, 140.4, 134.5, 129.8, 124.6, 121.7, 120.8, 120.7, 38.0, 35.8, 33.8, 31.7, 31.3, 29.9, 29.7 ppm.

**Compound 2b (R = <sup>i</sup>Pr).** Yield: 99%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.22 (d, 1H, *J* = 2.54 Hz, *im-H*), 7.05 (s, 2H, *Ar-H*), 6.76 (s, 1H, *J* = 2.50 Hz, *im-H*), 4.62 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.47 (d, 3H, *J* = 6.71 Hz, CHCH<sub>3</sub>), 1.46 (d, 3H, *J* = 6.61 Hz, CHCH<sub>3</sub>), 1.26 (br s, 18H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.6, 140.5, 134.4, 130.0, 124.4, 121.8, 115.4, 53.2, 35.8, 33.8, 31.6, 30.0, 24.1, 23.4 ppm.

**Compound 2c (R = Ph).** Yield: 99%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.40 (s, 3H, *Ar-H*), 7.35 (s, 1H, *Ar-H*), 7.33 (s, 1H, *Ar-H*), 7.24 (d, 1H, *J* =

2.04 Hz, im-*H*), 7.22 (s, 1H, Ar-*H*), 7.12 (s, 1H, Ar-*H*), 6.82 (d, 1H, *J* = 2.02 Hz, im-*H*), 1.29 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.7, 140.6, 139.9, 134.4, 129.9, 129.7, 128.0, 125.1, 124.6, 123.7, 121.5, 120.4, 120.3, 35.8, 33.8, 31.7, 30.0, 29.6 ppm.

**Compound 2d** (*R* = *Mes*). Yield: 99%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.21 (d, 1H, *J* = 2.30 Hz, im-*H*), 7.12 (s, 1H, Ar-*H*), 7.02 (s, 1H, Ar-*H*), 6.95 (s, 1H, Ar-*H*), 6.85 (s, 1H, Ar-*H*), 6.73 (d, 1H, *J* = 2.28 Hz, im-*H*), 2.40 (s, 3H, Ar-CH<sub>3</sub>), 2.08 (s, 3H, Ar-CH<sub>3</sub>), 1.80 (s, 3H, Ar-CH<sub>3</sub>), 1.30 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.29 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.6, 140.6, 138.7, 135.9, 135.3, 135.1, 134.3, 129.3, 129.0, 124.6, 121.8, 35.8, 33.8, 31.6, 30.4, 21.0, 19.0, 18.0 ppm.

**General Procedures for Preparation of the *o*-Aryloxo-NHC Ligated *p*-Cymene Ruthenium Complexes 3a–d.** To a solution of [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (0.304 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added a solution of AgL (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub>, and the resultant red solution was stirred at room temperature for 20 h. The mixture was subsequently filtered through Celite, and the red filtrate was evaporated to dryness under reduced pressure. After recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, complex 3 was obtained in a yield of ~99%.

**Compound 3a** (*R* = *Me*). Yield: 99%. Mp: 180 °C dec. Anal. Calcd for C<sub>28</sub>H<sub>39</sub>ClN<sub>2</sub>ORu: C, 60.47; H, 7.07; N, 5.04. Found: C, 60.36; H, 7.17; N, 5.03. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.27 (s, 1H, im-*H*), 7.02 (s, 2H, Ar-*H*), 6.89 (d, 1H, *J* = 1.80 Hz, im-*H*), 5.54 (d, 1H, *J* = 5.61 Hz, *p*-cymene-*CH*), 5.42 (d, 1H, *J* = 5.60 Hz, *p*-cymene-*CH*), 4.90 (d, 1H, *J* = 5.65 Hz, *p*-cymene-*CH*), 4.56 (d, 1H, *J* = 5.59 Hz, *p*-cymene-*CH*), 3.90 (s, 3H, NCH<sub>3</sub>), 2.16 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.97 (s, 3H, Ar-CH<sub>3</sub>), 1.50 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.25 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.94 (d, 3H, *J* = 6.75 Hz, CHCH<sub>3</sub>), 0.82 (d, 3H, *J* = 6.91 Hz, CHCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 174.5, 159.3, 140.8, 135.4, 129.7, 123.4, 120.9, 118.7, 113.9, 86.4, 82.1, 78.3, 37.9, 35.7, 33.9, 31.6, 30.2, 30.1, 30.0, 20.8, 18.7 ppm. HRMS (MALDI, *m/z*): calcd for C<sub>28</sub>H<sub>39</sub>ClN<sub>2</sub>ORu (*M* – Cl) 521.2107, found 521.2115.

**Compound 3b** (*R* = *iPr*). Yield 99%. Mp: 200 °C dec. Anal. Calcd for C<sub>30</sub>H<sub>43</sub>ClN<sub>2</sub>ORu: C, 61.68; H, 7.42; N, 4.80. Found: C, 61.46; H, 7.37; N, 5.03. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.38 (d, 1H, *J* = 1.98 Hz, im-*H*), 7.15 (d, 1H, *J* = 2.03 Hz, im-*H*), 7.04 (d, 1H, *J* = 2.43 Hz, Ar-*H*), 6.90 (d, 1H, *J* = 2.43 Hz, Ar-*H*), 5.59 (d, 1H, *J* = 5.65 Hz, *p*-cymene-*CH*), 5.43 (d, 1H, *J* = 5.68 Hz, *p*-cymene-*CH*), 5.13 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.92 (d, 1H, *J* = 5.70 Hz, *p*-cymene-*CH*), 4.57 (d, 1H, *J* = 5.73 Hz, *p*-cymene-*CH*), 2.12 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.02 (s, 3H, Ar-CH<sub>3</sub>), 1.58 (d, 3H, *J* = 6.86 Hz, CHCH<sub>3</sub>), 1.52 (d, 3H, *J* = 6.08 Hz, CHCH<sub>3</sub>), 1.51 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.93 (d, 3H, *J* = 6.81 Hz, CHCH<sub>3</sub>), 0.85 (d, 3H, *J* = 6.96 Hz, CHCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 174.0, 160.0, 140.8, 135.6, 130.1, 121.0, 119.4, 118.2, 114.1, 86.4, 82.8, 81.7, 78.0, 52.5, 35.7, 34.0, 31.7, 30.3, 24.5, 24.2, 23.6, 20.6, 18.8 ppm. HRMS (MALDI, *m/z*): calcd for C<sub>30</sub>H<sub>43</sub>ClN<sub>2</sub>ORu (*M* – Cl) 549.2420, found 549.2426.

**Compound 3c** (*R* = *Ph*). Yield: 99%. Mp: 185 °C dec. Anal. Calcd for C<sub>33</sub>H<sub>41</sub>ClN<sub>2</sub>ORu: C, 64.11; H, 6.68; N, 4.53. Found: C, 64.06; H, 6.56; N, 4.73. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.03 (d, 1H, *J* = 7.34 Hz, Ar-*H*), 7.50 (m, 4H, Ar-*H*), 7.25 (s, 1H, Ar-*H*), 7.06 (d, 1H, *J* = 1.90 Hz, im-*H*), 6.95 (d, 1H, *J* = 1.98 Hz, im-*H*), 5.47–3.86 (m, 4H, *p*-cymene-*CH*), 2.14 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.89 (s, 3H, Ar-CH<sub>3</sub>), 1.52 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.28 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.89 (d, 3H, *J* = 6.71 Hz, CHCH<sub>3</sub>), 0.78 (d, 3H, *J* = 6.90 Hz, CHCH<sub>3</sub>) ppm. HRMS (MALDI, *m/z*): calcd for C<sub>33</sub>H<sub>41</sub>ClN<sub>2</sub>ORu (*M* – Cl) 583.2265, found 583.2268.

**Compound 3d** (*R* = *Mes*). Yield: 99%. Mp: 165 °C dec. Anal. Calcd for C<sub>36</sub>H<sub>47</sub>ClN<sub>2</sub>ORu: C, 65.48; H, 7.17; N, 4.24. Found: C, 65.40; H, 7.11; N, 4.33. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.56 (d, 1H, *J* = 1.68 Hz, Ar-*H*), 7.17 (s, 1H, Ar-*H*), 7.07 (s, 1H, im-*H*), 7.03 (d, 1H, *J* = 2.18 Hz, im-*H*), 6.92 (s, 1H, Ar-*H*), 6.91 (s, 1H, Ar-*H*), 5.75–4.76 (m, 4H, *p*-cymene-*CH*), 2.68 (t, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.44 (s, 3H, Ar-CH<sub>3</sub>), 2.35 (s, 3H, Ar-CH<sub>3</sub>), 2.16 (s, 3H, Ar-CH<sub>3</sub>), 1.79 (s, 3H, Ar-CH<sub>3</sub>), 1.49 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (s, 6H, Ar-CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 173.0, 155.8, 139.9, 139.8, 138.7, 134.5, 129.3, 128.9, 121.9, 121.5, 121.1, 118.9, 113.5, 81.1, 80.4, 35.2, 33.9, 31.6, 31.5, 31.2, 29.9, 29.5, 21.1, 18.2, 17.7 ppm. HRMS (MALDI, *m/z*): calcd for C<sub>36</sub>H<sub>47</sub>ClN<sub>2</sub>ORu (*M* – Cl) 625.2735, found 625.2736.

**Crystallographic Studies.** Single crystals suitable for X-ray diffraction were obtained from CH<sub>2</sub>Cl<sub>2</sub>/ether for 3b. Data collections were performed on a Rigaku Saturn 70 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). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least squares. All calculations were performed by using the SHELXL-97 program system. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations.

**NBE Polymerization.** In a typical procedure, 1.0 g of NBE in 30.0 mL of toluene was added into a flask (100 mL) with stirring under an Ar atmosphere. After the mixture was kept at the desired temperature for 3–5 min, the catalyst (5  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was injected into the flask via syringe, and the reaction was started. To stop the polymerization, a 2-ethyl vinyl ether/BHT (2,6-di-*tert*-butyl-4-methylphenol) solution in CHCl<sub>3</sub> was added. The reaction mixture was then poured into MeOH (50 mL) to precipitate the polymer. The polymer was isolated upon filtration and analyzed gravimetrically by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy and GPC (gel permeation chromatography).

**NBE and COE Copolymerization.** In a typical procedure, the NBE/COE mixture with different ratios in 10.0 mL of toluene was added into a flask (100 mL) with stirring under an Ar atmosphere. After the mixture was kept at the desired temperature for 3–5 min, initiator 3d (3.3 mg, 5  $\mu$ mol) dissolved in 1.0 mL of CH<sub>2</sub>Cl<sub>2</sub> was injected into the flask via syringe, and the reaction was started. The reaction mixture was stirred for 12 h. Then the reaction was stopped by the addition of a 2-ethyl vinyl ether/BHT (2,6-di-*tert*-butyl-4-methylphenol) solution in CHCl<sub>3</sub>. The polymer was precipitated by the dropwise addition of the reaction mixture into ethanol. The polymer was collected by filtration and analyzed gravimetrically by <sup>13</sup>C NMR spectroscopy and GPC (gel permeation chromatography).

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

A CIF file giving X-ray structural information for 3b and figures giving <sup>1</sup>H and <sup>13</sup>C NMR spectra for complexes 2a–d and 3a–d and GPC curves and NMR spectra for the obtained polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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