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o-Aryloxide-N-heterocyclic Carbenes: Efficient Synthesis of the Proligands and Their *p*-Cymene Ruthenium Complexes

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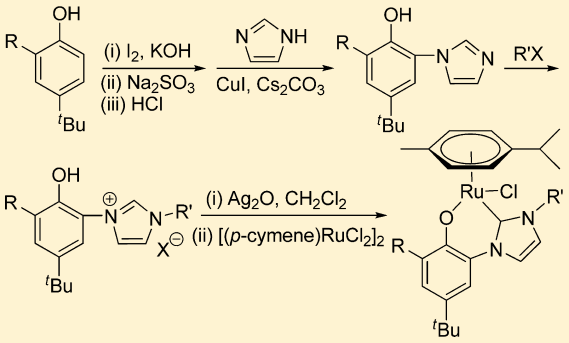
Supporting Information

ABSTRACT: An efficient method to synthesize *o*-hydroxyaryl-substituted imidazoles (2-OH-3-R-5-^{t}BuC$_6$H$_2$)(C$_3$H$_3$N$_2$) [R = ^{t}Bu (**1a**), H (**1b**)] was developed through copper-catalyzed C−N bond formation. Treatment of **1a** or **1b** with a halohydrocarbon in refluxing toluene afforded a series of *o*-hydroxyaryl imidazolinium proligands **2a−h** in high yields. Reactions of proligands **2a−h** with Ag_2O and [(*p*-cymene)$RuCl_2$]$_2$ gave the corresponding *o*-aryloxide-N-heterocyclic carbene ligated *p*-cymene ruthenium complexes **3a−h**. All the imidazolium salts and ruthenium complexes were fully characterized by ^{1}H and ^{13}C NMR spectra, elemental analysis, and high-resolution mass spectrometry. Without the cocatalyst or irradiation, these complexes can efficiently catalyze norbornene ring-opening metathesis polymerization. Notably, the structures of the catalysts were found to have significant effects on the catalytic activity and the properties of obtained polymers.

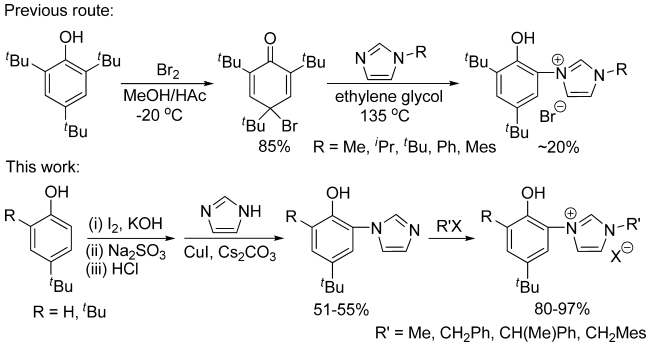


INTRODUCTION

In the past decades, the chemistry of N-heterocyclic carbenes (NHCs) as well as their metal complexes has received much attention in the field of organometallics and catalysis since the precursory work of Arduengo.[1] By introducing an NHC ligand into a Grubbs I catalyst, the resulting Grubbs II catalyst shows higher activities for olefin metathesis reaction, excellent functional group tolerance, and better thermal stability.[2] These NHC-Ru complexes as well as Ru-benzylidene catalysts lead to excellent olefin metathesis catalysts. They are widely applied in constructing a variety of molecules.[3] Different from the well-defined ruthenium catalysts containing a ruthenium−carbon double bond, the ill-defined ruthenium catalysts do not have an alkylidene fragment. They are generally commercially available and exhibit comparable performance to the well-defined catalysts or even better results.[4] Since Noels and co-workers first reported that (*p*-cymene)$RuCl_2(PCy_3)$ can efficiently catalyze the ring-opening metathesis polymerization (ROMP) of norbornene,[5] *p*-cymene-based catalysts with various types of ligands including phosphines,[6,7] bidentate Schiff bases,[8,9] and NHC ligands[10,11] have been widely investigated so far.

Recently, transition-metal complexes with anion-tethered NHC ligands have received much attention.[12] As an anchor, the featured anion groups can enhance the bond between the NHC ligands and metal atoms and inhibit the possibility of ligand dissociation. In the previous work, we designed and synthesized a series of *o*-hydroxyaryl NHC proligands and their transition-metal complexes.[13] Among them, the cymene or benzene Ru complexes can efficiently catalyze the ROMP of norbornene and alternating copolymerization of norbornene and cyclooctene without any cocatalyst or irradiation conditions.[13e,f] However, the synthetic methods for the proligands of catalysts are not very efficient (Scheme 1).[13a,b] It may limit their further application. Hence, it is vitally important to look for a new way to synthesize the proligands and in turn develop various transition-metal catalysts bearing this ligand framework. In this work, we report an efficient method to synthesize the *o*-

Scheme 1. Synthetic Routes of the Proligands



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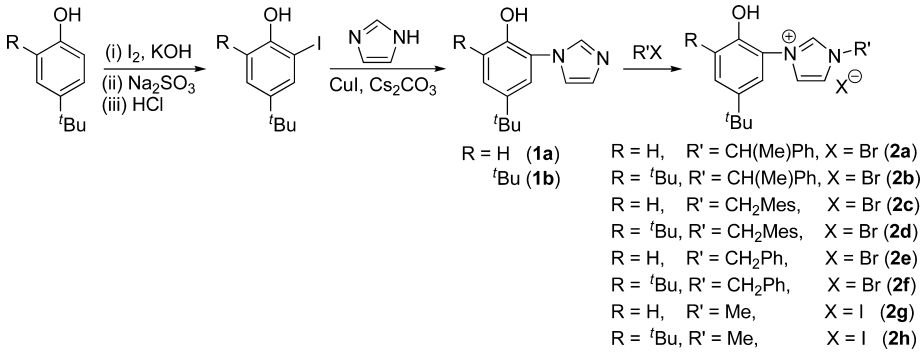
Scheme 2. Synthesis of *o*-Hydroxyaryl Imidazolium Proligands 2a−h



hydroxyaryl imidazolium proligands through copper-catalyzed C−N bond formation and nucleophilic substitution with halohydrocarbon (Scheme 1). The corresponding *p*-cymene ruthenium complexes featuring these *o*-aryloxide-NHC ligands were also prepared and used to catalyze the ROMP of norbornene (NBE) without any cocatalyst or irradiation conditions.

RESULTS AND DISCUSSION

Synthesis of *o*-Hydroxyaryl Imidazolium Proligands. In 2007, we reported the synthesis of the *o*-hydroxyaryl imidazolium proligand;[13a,b] however, the reactions were relatively complicated and the yields were very low, which extremely discouraged their wide research and usage. Thus, we herein develop a new, simple, and efficient method, which is different from the well-established approach in our laboratory.

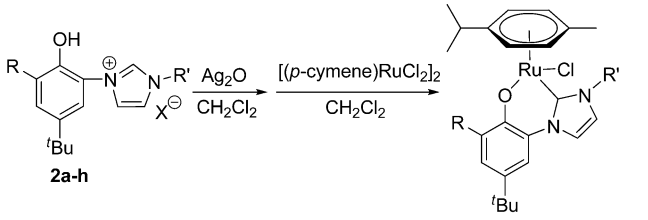
As shown in Scheme 2, upon dropwise addition of a methanolic iodine solution to a solution of 2,4-di-*tert*-butylphenol in methanol containing KOH at room temperature,[14a] the reaction mixture became light yellow. It should be noted that if the reactant is 4-*tert*-butylphenol, the iodine was added at 0 °C. Then the mixture was washed with an aqueous Na_2SO_3 solution, followed by acidification, extraction, and eventually evaporation to leave an iodophenol compound as a yellow solid. This process is very simple, and the yield is nearly quantitative. The product can be directly used without further purification in the next step. The second step is a common C−N coupling reaction catalyzed by CuI. In short, materials of the reaction are cheap, and the yield is high (51−55%). So it can be synthesized in large scale. Then *o*-hydroxyaryl imidazolium salts **2a−h** were synthesized by the reactions of **1a** or **1b** with a halohydrocarbon in refluxing toluene in 80−97% yields.[14b]

Proligands **2a−h** are soluble in CH_2Cl_2, $CHCl_3$, and CH_3OH, but insoluble in diethyl ether and hexane. They have been fully characterized by ^1H and ^{13}C NMR spectra and high-resolution mass spectrometry (HRMS). All the ^1H NMR spectra of **2a−h** display a characteristic singlet at 9−10 ppm for the imidazolium proton, as reported in the previous literature for similar imidazolium salts.

Synthesis of *o*-Aryloxide-NHC Ruthenium Complexes. Following the procedures as described previously by our group,[13] **3a−h** were synthesized by the reactions of proligands **2a−h** with 3 equiv of Ag_2O and 1 equiv of $[(p\text{-cymene})RuCl_2]_2$ in high yields (Scheme 3).

The ruthenium complexes **3b**, **3d**, **3f**, and **3h** are very stable in air, but **3a**, **3c**, **3e**, and **3g** turn dark when exposed to air for a few hours. They are all soluble in 1,2-dimethoxyethane, CH_2Cl_2, THF, acetone, dioxane, and toluene, but insoluble in

Scheme 3. Synthesis of *o*-Aryloxide-NHC Ruthenium Complexes 3a−h



diethyl ether and other hydrocarbon solvents. All of them have been fully characterized by ^1H and ^{13}C NMR, HRMS, and elemental analysis. In their ^1H NMR spectra the characteristic signals of the phenol and imidazole protons for the proligands disappeared completely. The signals of the cymene protons in the ^1H NMR spectra and the carbene carbons in the ^{13}C NMR spectra appeared at 4.50−5.50 ppm and about 175.0 ppm, respectively. They are similar to those of the Ru-cymene NHC complexes reported previously.[13,15] HRMS and elemental analysis results supported their structures. Single-crystal X-ray diffraction analysis further confirmed the structures of **3b**. The unit cell contains two crystallographically independent molecules, and the structure description is for one of them (Figure 1). The Ru−C(carbene) and Ru−O bond lengths are 2.036(2) and 2.0946(14) Å, respectively. They are similar to those in other *o*-aryloxide-N-heterocyclic ruthenium complexes.[13]

ROMP of NBE. ROMP is a very powerful method for the preparation of polymers with narrow polydispersities.[3a,16,17] To study the structure−property relationship of catalysts, the ROMP of NBE with **3a−g** was studied, while the polymer data of **3h** were reported by our group previously.[13e] The polymerization results are shown in Table 1. It is clear that without any cocatalyst all the ruthenium complexes **3a−g** exhibit moderate or high activity toward the ROMP of norbornene at 85 °C. Much to our surprise, the introduction of *tert*-butyl at the *ortho* position of the aryloxide could decrease the activity, but results in a significant increase in the molecular weight of the obtained polymer (entries 2, 4, 6, 8). The substituents of imidazole also have an effect on the catalytic

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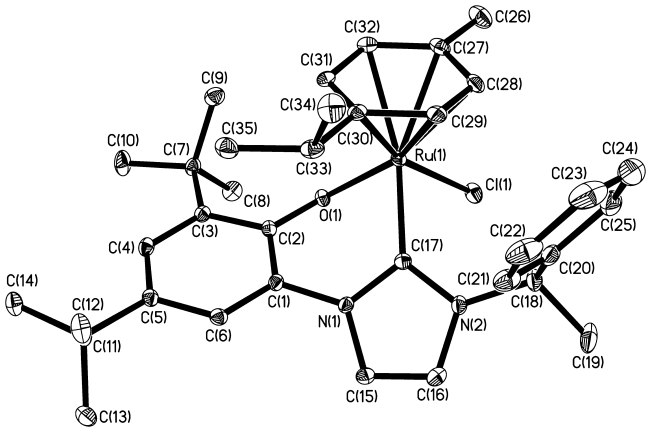


Figure 1. ORTEP diagram of **3b** (one of two independent molecules in the unit cell is shown). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): Ru(1)−C(17) 2.036(2), Ru(1)−O(1) 2.0946(14), Ru(1)−Cl(1) 2.4184(7), C(17)−Ru(1)−O(1) 82.06(7), C(17)−Ru(1)−Cl(1) 86.33(6), O(1)−Ru(1)−Cl(1) 85.50(4), N(1)−C(17)−N(2) 104.66(18).

Table 1. ROMP of NBE with 3a−h[a]

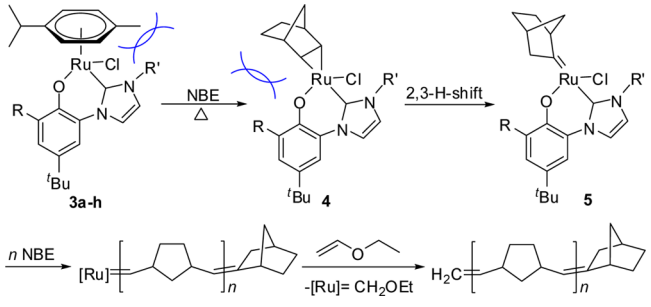
entry	cat.	yield (%)	M_n (×10^3)	PDI	*cis* (%)
1	**3a**	85	372	1.94	27
2	**3b**	44	476	2.88	20
3	**3c**	70	424	3.33	34
4	**3d**	57	1571	1.81	25
5	**3e**	68	470	1.63	21
6	**3f**	30	572	3.05	28
7	**3g**	30	454	2.56	26
8[b]	**3h**	29	902	2.02	39

[a]Polymerization conditions: In 30 mL of toluene; 1.0 g of NBE; [cat.] = 0.167 mmol L^{-1}; 85 °C; 3 h; GPC versus polystyrene standards. [b]The data are from our previous work.[13e]

activity. The rough rule is that the bulkier the N-bonded alkyl substituent, the higher the yield the resultant polymer.

Following a similar mechanism for the *p*-cymene-Ru system reported previously,[3e,8a,9,13] the active ruthenium carbene species might be generated by the release of a *p*-cymene ligand from **3**, the coordination of NBE to ruthenium, and then a 2,3-hydrogen shift (Scheme 4). The bulky steric effect of the N-bonded alkyl substituent may increase the interaction with the *p*-cymene group and promote the release of a *p*-cymene ligand and the formation of the active ruthenium species **5**, which lead to the high yield of the resultant polymer. When R is *tert*-butyl, the interaction between *tert*-butyl and the NBE ligand may decrease the stability of active species **4** and suppress its formation, which leads to the low yield of the resultant polymer.

Scheme 4. Proposed Catalytic Mechanism



CONCLUSION

In conclusion, we have successfully developed an efficient route to synthesize *o*-hydroxyaryl imidazolinium proligands and synthesized a series of corresponding *o*-aryloxide-N-heterocyclic carbene *p*-cymene-Ru complexes. These complexes can efficiently catalyze the ROMP of NBE without any cocatalyst. Notably, introduction of a *tert*-butyl at the *ortho* position of the aryloxide could decrease the activity, but results in a significant increase in the molecular weight (up to 1.57 × 10^6) of the obtained polymer. The steric effect of the substituting group at imidazole may improve the activity. The bulkier the N-bonded alkyl substituent, the higher the yield the resultant polymer.

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 using. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer. HRMS were carried out on Agilent 6520 Q-TOF mass spectrometers. Elemental analyses were performed on a PerkinElmer 240C analyzer. The molecular weights and molecular weight distribution of entries 1 and 5 in Table 1 were obtained on GPC [Waters 1525 liquid chromatography connected with styragel GPC columns (HT 2, 3, 4 THF) and a Waters 2414 differential refractometer], while the others were obtained on GPC [Waters 510 liquid chromatography connected with four styragel GPC columns (guard, 10^3 Å, 10^4 Å, 10^5 Å) and a Waters 410 differential refractometer]. The eluent of all polymers is THF.

Synthesis of 2,4-Di-*tert*-butyl-6-(1*H*-imidazol-1-yl)phenol (1b). To a stirred solution of 2,4-di-*tert*-butylphenol (6.18 g, 30.0 mmol) and KOH (6.72 g, 120.0 mmol) in methanol (60 mL) at room temperature was dropwisely added a solution of I_2 (7.61 g, 30.0 mmol) in methanol (50 mL) over a period of ca. 1 h. After stirring for 30 min, a solution of Na_2SO_3 (3.78 g, 30.0 mmol) in 30 mL of water was added to quench unreacted I_2. The reaction mixture was acidified with HCl until pH = 5 and extracted with CH_2Cl_2. Removal of solvent under reduced pressure gave the crude product 2,4-di-*tert*-butyl-6-iodophenol. A mixture of the above crude product (30 mmol), imidazole (2.50 g, 36 mmol), Cs_2CO_3 (19.5 g, 60 mmol), and CuI (570 mg, 3 mmol) in 120 mL of DMSO was stirred under an argon atmosphere at 120 °C for 36 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water again, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to get the crude product. Purification by column chromatography afforded **1b** as a white solid. Yield: 51%. Mp: 162−163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H, im-*H*), 7.41 (d, 1H, J = 2.36 Hz, im-*H*), 7.10 (s, 1H, Ar-*H*), 7.05 (s, 1H, im-*H*), 6.96 (d, 1H, J = 2.35 Hz, im-*H*), 1.48 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 142.2, 139.2, 128.6, 125.4, 124.7, 121.4, 35.5, 34.3, 31.4, 29.7 ppm. HRMS (ESI, m/z): calcd for $C_{17}H_{24}N_2O$ [M + H]$^+$ 273.1967, found 273.1969.

Synthesis of 4-*tert*-Butyl-2-(1*H*-imidazol-1-yl)phenol (1a). This compound was prepared in a similar manner to that described for **1b**, except that a solution of I_2 in methanol was dropped into the mixture in an ice water bath. Yield: 55%. Mp: 189−190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H, im-*H*), 7.28 (d, 1H, J = 8.80 Hz, Ar-*H*), 7.21 (s, 1H, Ar-*H*), 7.18 (d, 1H, J = 1.60 Hz, Ar-*H*), 7.08−7.12 (m, 2H, im-*H*), 1.30 (s, 9H, $C(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 137.3, 126.8, 125.9, 123.9, 121.9, 120.1, 117.2, 33.8, 31.1 ppm. HRMS (ESI, m/z): calcd for $C_{13}H_{16}N_2O$ [M + H]$^+$ 217.1341, found 217.1340.

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General Procedures for Synthesis of Proligands 2a−h. A mixture of *o*-hydroxyarylimidazole and 1.5 equiv of halohydrocarbon was refluxed for 15 h in toluene. Recrystallization from CH_2Cl_2/Et_2O gave the product as a white solid.

Compound ***2a***. Yield: 87%. Mp: 190−191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H, NC*H*N), 7.65−7.48 (m, 4H, Ar-*H*), 7.41 (m, 4H, Ar-*H*), 7.28 (d, 1H, J = 5.2 Hz, im-*H*), 7.15 (d, 1H, J = 2.08 Hz, im-*H*), 6.10−6.13 (m, 1H, NC*H*), 2.01 (m, 3H, CHCH_3), 1.26 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 144.1, 137.6, 134.2, 129.7, 128.6, 127.3, 123.7, 121.4, 120.3, 119.0, 60.2, 34.4, 31.5, 21.3 ppm. HRMS (ESI, m/z): calcd for $C_{21}H_{25}BrN_2O$ $[M - Br]^+$ 321.1967, found 321.1966.

Compound ***2b***. Yield: 81%. Mp: 136−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H, NC*H*N), 8.24 (s, 1H, Ar-*H*), 7.54 (s, 1H, Ar-*H*), 7.53 (s, 1H, Ar-*H*), 7.40−7.43 (m, 4H, Ar-*H*), 7.29 (s, 1H, im-*H*), 7.01 (d, 1H, J = 2.08 Hz, im-*H*), 5.78−5.83 (m, 1H, NC*H*), 2.03−2.06 (m, 3H, CHCH_3), 1.41 (s, 9H, C(CH_3)$_3$), 1.27 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 144.4, 143.1, 137.7, 136.5, 129.5, 127.5, 126.3, 126.0, 123.8, 121.0, 119.8, 60.6, 35.7, 34.6, 31.4, 30.0, 21.1 ppm. HRMS (ESI, m/z): calcd for $C_{25}H_{33}BrN_2O$ $[M - Br]^+$ 377.2593, found 377.2595.

Compound ***2c***. Yield: 82%. Mp: 200−201 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H, NC*H*N), 9.46 (s, 1H, Ar-O*H*), 7.53 (dd, 1H, Ar-*H*), 7.43 (s, 1H, Ar-*H*), 7.24 (s, 1H, Ar-*H*), 7.22 (s, 1H, Ar-*H*), 7.15 (d, 1H, J = 7.30 Hz, Ar-*H*), 6.90 (s, 2H, im-*H*), 5.67 (s, 2H, NCH_2), 2.27 (s, 9H, ArCH_3), 1.24 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 143.8, 140.0, 138.3, 135.8, 130.0, 129.0, 128.5, 128.2, 125.3, 125.2, 123.2, 121.4, 121.0, 121.0, 118.8, 48.5, 34.3, 31.4, 21.1, 19.9 ppm. HRMS (ESI, m/z): calcd for $C_{23}H_{29}BrN_2O$ $[M - Br]^+$ 349.2280, found 349.2284.

Compound ***2d***. Yield: 83%. Mp: 237−238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H, NC*H*N), 7.42 (s, 1H, Ar-*H*), 7.33 (s, 1H, Ar-*H*), 7.29 (s, 1H, Ar-*H*), 6.94 (s, 1H, Ar-*H*), 6.93 (s, 2H, im-*H*), 5.59 (s, 2H, NCH_2), 2.38 (s, 6H, ArCH_3), 2.29 (s, 3H, ArCH_3), 1.38 (s, 9H, C(CH_3)$_3$), 1.27 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 143.9, 142.4, 139.9, 138.7, 136.7, 129.9, 126.3, 125.3, 125.2, 123.6, 121.8, 119.7, 48.5, 35.7, 34.5, 31.4, 29.8, 21.1, 20.3 ppm. HRMS (ESI, m/z): calcd for $C_{27}H_{37}BrN_2O$ $[M - Br]^+$ 405.2906, found 405.2912.

Compound ***2e***. Yield: 97%. Mp: 125−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H, NC*H*N), 7.53 (d, 1H, J = 3.19 Hz, Ar-*H*), 7.47 (d, 4H, J = 8.50 Hz, Ar-*H*), 7.26 (s, 1H, Ar-*H*), 7.26 (s, 1H, Ar-*H*), 7.18−7.22 (m, 3H, Ar-*H*), 7.12 (d, 2H, J = 4.49 Hz, im-*H*), 5.61 (s, 2H, NCH_2), 1.17 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 143.9, 135.9, 135.8, 133.0, 129.5, 129.4, 129.0, 128.4, 128.2, 125.3, 123.2, 121.8, 121.2, 118.5, 65.8, 34.3, 31.4 ppm. HRMS (ESI, m/z): calcd for $C_{20}H_{23}BrN_2O$ $[M - Br]^+$ 307.1810, found 307.1815.

Compound ***2f***. Yield: 83%. Mp: 219−220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H, NC*H*N), 8.17 (s, 1H, Ar-O*H*), 7.53 (s, 3H, Ar-*H*), 7.40 (d, 4H, J = 8.09 Hz, Ar-*H*), 7.29 (s, 1H, im-*H*), 7.00 (s, 1H, im-*H*), 5.55 (s, 2H, NCH_2), 1.37 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 147.2, 144.0, 142.5, 142.1, 139.9, 137.2, 133.1, 132.4, 132.4, 129.7, 129.6, 129.5, 126.4, 125.6, 125.1, 124.3, 123.8, 122.3, 122.3, 120.1, 115.2, 53.8, 35.7, 34.5, 31.4, 39.8 ppm. HRMS (ESI, m/z): calcd for $C_{24}H_{31}BrN_2O$ $[M - Br]^+$ 363.2436, found 363.2440.

Compound ***2g***. Yield: 97%. Mp: 292−295 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H, NC*H*N), 8.30 (s, 1H, Ar-*H*), 7.67 (s, 1H, Ar-*H*), 7.53 (d, 1H, J = 8.58 Hz, Ar-*H*), 7.43 (s, 1H, im-*H*), 7.32 (s, 1H, im-*H*), 4.14 (s, 3H, NCH_3), 1.24 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 144.5, 136.3, 128.6, 125.7, 123.2, 121.7, 121.4, 118.5, 37.8, 34.4, 31.4 ppm. HRMS (ESI, m/z): calcd for $C_{14}H_{19}IN_2O$ $[M - I]^+$ 231.1497, found 231.1499.

Compound ***2h***. Yield: 94%. Mp: >300 °C. ^{1}H NMR (400 MHz, DMSO): δ 9.43 (s, 1H, Ar-O*H*), 9.14 (s, 1H, NC*H*N), 7.91 (m, 1H, Ar-*H*), 7.88 (m, 1H, Ar-*H*),7.42 (d, 1H, J = 2.40 Hz, im-*H*), 7.86 (d, 1H, J = 2.40 Hz, im-*H*), 3.91 (s, 3H, NCH_3), 1.41 (s, 9H, C(CH_3)$_3$), 1.28 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR (100 MHz, DMSO): δ 147.2, 142.2, 138.1, 125.1, 124.3, 124.0, 123.4, 121.5, 35.7, 35.0, 34.0, 30.1, 29.4 ppm. HRMS (ESI, m/z): calcd for $C_{18}H_{27}IN_2O$ $[M - I]^+$ 287.2123, found 287.2126.

General Procedures for Synthesis of Complexes 3a−g. A solution of **2** and 3 equiv of Ag_2O in CH_2Cl_2 was stirred at room temperature in the dark for 12 h and then filtered over a pad of Celite. The filtrate was added to a solution of 1 equiv of $[(p\text{-cymene})RuCl_2]_2$ in CH_2Cl_2. The resultant red solution was stirred for 48 h under exclusion of light. After filtration over a pad of Celite and removal of the solvent under reduced pressure the crude product was obtained. Recrystallization from CH_2Cl_2/hexane gave compounds **3** as brown crystals.

Compound ***3a***. Yield: 71%. Mp: >300 °C. Anal. Calcd for $C_{31}H_{37}ClN_2ORu$: C, 63.09; H, 6.32; N, 4.75. Found: C, 62.95; H, 6.50; N, 4.83. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 2H, Ar-*H*), 7.42 (d, J = 7.0 Hz, 2H, Ar-*H*), 7.35 (s, 2H, Ar-*H*), 7.26−7.22 (m, 2H, Ar-*H*), 7.12 (s, 1H, Ar-*H*), 7.05 (s, 2H, im-*H*), 6.43−6.44 (m, 1H, NC*H*), 5.38 (s, 1H, *p*-cymene-C*H*), 4.83 (s, 1H, *p*-cymene-C*H*), 4.73 (s, 1H, *p*-cymene-C*H*), 4.40 (s, 1H, *p*-cymene-C*H*), 1.94 (s, 3H, CH-CH_3), 1.91−1.93 (m, 1H, C*H*(CH$_3$)$_2$), 1.85 (d, J = 6.5 Hz, CH-CH_3), 1.29 (s, 9H, C(CH_3)$_3$), 0.75 (d, J = 6.2 Hz, 6H, CH(CH_3)$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 144.2, 138.0, 129.9, 129.1, 127.4, 125.1, 121.2, 120.4, 118.6, 116.3, 88.0, 84.4, 80.7, 77.4, 76.7, 59.6, 33.9, 31.7, 30.3, 23.7, 23.1, 22.7, 21.1, 18.4, 14.1 ppm. HRMS (ESI, m/z): calcd for $C_{31}H_{37}ClN_2ORu$ $[M - Cl]^+$ 555.1949, found 555.1952.

Compound ***3b***. Yield: 95%. Mp: >300 °C. Anal. Calcd for $C_{35}H_{45}ClN_2ORu$: C, 65.05; H, 7.02; N, 4.33. Found: C, 65.03; H, 7.08; N, 4.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 1H, J = 1.53 Hz, Ar-*H*), 7.42−7.45 (m, 2H, Ar-*H*), 7.39 (d, 1H, J = 1.45 Hz, Ar-*H*), 7.32−7.36 (m, 1H, Ar-*H*), 7.30 (s, 1H, Ar-*H*), 7.28 (s, 1H, Ar-*H*), 7.06 (d, 1H, J = 2.13 Hz, im-*H*), 6.99 (d, 1H, J = 2.02 Hz, im-*H*), 6.47−6.52 (m, 1H, NC*H*), 5.30 (d, 1H, J = 1.93 Hz, *p*-cymene-C*H*), 4.84 (d, 1H, J = 3.65 Hz, *p*-cymene-C*H*), 4.77 (s, 1H, *p*-cymene-C*H*), 4.30 (d, 1H, J = 4.45 Hz, *p*-cymene-C*H*), 1.99 (s, 3H, Ar-CH_3), 1.98 (m, 1H, C*H*(CH$_3$)$_2$), 1.85 (d, 3H, J = 7.08 Hz, CH-CH_3), 1.52 (s, 9H, C(CH_3)$_3$), 1.29 (s, 9H, C(CH_3)$_3$), 0.81 (d, 3H, J = 4.80 Hz, CH-CH_3), 0.70 (d, 3H, J = 5.90 Hz, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 159.2, 143.5, 134.0, 134.7, 129.2, 128.1, 126.4, 124.1, 120.3, 119.3, 118.4, 113.3, 58.5, 34.8, 33.1, 30.7, 29.3, 29.2, 23.0, 21.9, 20.2, 17.8 ppm. HRMS (MALDI, m/z): calcd for $C_{35}H_{45}ClN_2ORu$ $[M - Cl]^+$ 611.2575, found 611.2573.

Compound ***3c***. Yield: 96%. Mp: >300 °C. Anal. Calcd for $C_{33}H_{41}ClN_2ORu$: C, 64.11; H, 6.68; N, 4.53. Found: C, 64.23; H, 6.88; N, 4.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H, Ar-*H*), 7.30 (s, 1H, Ar-*H*), 7.24 (s, 1H, im-*H*), 7.18 (s, 1H, Ar-*H*), 6.67 (s, 1H, im-*H*), 6.20 (dd, 1H, NC*H*), 5.94 (d, 1H, J = 5.50 Hz, *p*-cymene-C*H*), 5.69 (d, 1H, J = 5.60 Hz, *p*-cymene-C*H*), 5.35 (dd, 1H, NC*H*), 5.30 (d, 1H, J = 5.74 Hz, *p*-cymene-C*H*), 5.02 (d, 1H, J = 5.64 Hz, *p*-cymene-C*H*), 2.55 (d, 9H, J = 3.95 Hz, ArCH_3), 2.39 (s, 1H, C*H*(CH$_3$)$_2$), 2.28 (s, 3H, Ar-CH_3), 1.48 (s, 9H, C(CH_3)$_3$), 1.15 (d, 3H, J = 6.92 Hz, CH-CH_3), 1.11 (d, 3H, J = 6.77 Hz, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.7, 137.8, 128.7, 128.5, 126.7, 123.3, 120.3, 119.5, 116.0, 115.1, 102.1, 101.9, 87.6, 83.7, 79.5, 78.7, 52.8, 48.0, 32.9, 30.7, 30.6, 29.5, 28.3, 22.8, 20.1, 19.6, 19.0, 17.5 ppm. HRMS (MALDI, m/z): calcd for $C_{33}H_{41}ClN_2ORu$ $[M - Cl]^+$ 583.2262, found 583.2260.

Compound ***3d***. Yield: 97%. Mp: >300 °C. Anal. Calcd for $C_{37}H_{49}ClN_2ORu$: C, 65.90; H, 7.32; N, 4.15. Found: C, 65.83; H, 7.48; N, 4.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 1H, Ar-*H*), 7.19 (s, 1H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 6.89 (s, 1H, im-*H*), 6.43 (s, 1H, im-*H*), 5.96 (dd, 1H, NC*H*), 5.72 (d, 1H, J = 5.46 Hz, *p*-cymene-C*H*), 5.57 (d, 1H, J = 5.55 Hz, *p*-cymene-C*H*), 5.17 (dd, 1H, NC*H*), 5.04 (d, 1H, J = 5.61 Hz, *p*-cymene-C*H*), 4.64 (d, 1H, J = 5.61 Hz, *p*-cymene-C*H*), 2.35 (s, 6H, Ar-CH_3), 2.33 (s, 3H, Ar-CH_3), 2.17 (s, 1H, C*H*(CH$_3$)$_2$), 2.12 (s, 3H, Ar-CH_3), 1.54 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$), 0.95 (d, 3H, J = 6.71 Hz, CH-CH_3), 0.86 (d, 3H, J = 6.88 Hz, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 158.8, 139.9, 137.7, 134.7, 129.2, 128.5, 126.8, 120.3, 119.3, 116.7, 113.2, 85.8, 82.5, 80.5, 47.8, 34.8, 33.0, 30.7, 29.4, 22.7, 20.1, 19.7, 19.0, 17.9 ppm. HRMS (MALDI, m/z): calcd for $C_{37}H_{49}ClN_2ORu$ $[M - Cl]^+$ 639.2888, found 639.2890.

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Compound ***3e***. Yield: 44%. Mp: >300 °C. Anal. Calcd for $C_{30}H_{35}ClN_2ORu$: C, 62.54; H, 6.12; N, 4.86. Found: C, 62.43; H, 6.18; N, 4.75. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 1H, Ar-*H*), 7.39−7.43 (m, 2H, Ar-*H*), 7.33−7.36 (m, 3H, Ar-*H*), 7.08 (s, 2H, *im*-*H*), 7.04 (s, 1H, Ar-*H*), 7.00 (s, 1H, Ar-*H*), 5.71 (d, 1H, J = 15.87 Hz, NC*H*), 5.51 (d, 1H, J = 5.19 Hz, *p*-cymene-C*H*), 5.43 (d, 1H, J = 15.86 Hz, NC*H*), 5.05 (d, 1H, J = 5.71 Hz, *p*-cymene-C*H*), 4.95 (d, 1H, J = 5.68 Hz, *p*-cymene-C*H*), 4.55 (d, 1H, J = 5.68 Hz, *p*-cymene-C*H*), 2.04−2.10 (m, 1H, C*H*$(CH_3)_2$), 1.97 (s, 3H, ArCH_3), 1.28 (s, 9H, C$(CH_3)_3$), 0.83 (d, 6H, J = 6.88 Hz, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 136.4, 128.0, 127.0, 126.1, 123.4, 122.1, 120.3, 117.6, 115.2, 101.4, 87.5, 83.4, 79.7, 78.6, 53.4, 32.9, 30.6, 29.4, 22.2, 20.0, 17.4 ppm. HRMS (MALDI, m/z): calcd for $C_{30}H_{35}ClN_2ORu$ $[M - Cl]^+$ 541.1793, found 541.1791.

Compound ***3f***. Yield: 98%. Mp: >300 °C. Anal. Calcd for $C_{34}H_{43}ClN_2ORu$: C, 64.59; H, 6.88; N, 4.43. Found: C, 64.43; H, 6.88; N, 4.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.42 (m, 6H, Ar-*H*), 7.07 (s, 1H, Ar-*H*), 7.00 (s, 1H, *im*-*H*), 6.96 (s, 1H, *imH*), 5.80 (dd, 1H, NC*H*), 5.45 (s, 1H, NC*H*), 5.43 (d, 1H, J = 6.10 Hz, *p*-cymene-C*H*), 5.16 (d, 1H, J = 4.12 Hz, *p*-cymene-C*H*), 4.90 (d, 1H, J = 4.91 Hz, *p*-cymene-C*H*), 4.84 (d, 1H, J = 5.73 Hz, *p*-cymene-C*H*), 2.15 (s, 1H, C*H*$(CH_3)_2$), 2.00 (s, 3H, ArCH_3), 1.52 (s, 9H, C$(CH_3)_3$), 1.29 (s, 9H, C$(CH_3)_3$), 0.94 (d, 3H, J = 6.42 Hz, CH-CH_3), 0.79 (d, 3H, J = 6.19 Hz, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 159.9, 141.1, 137.5, 135.7, 130.0, 129.0, 128.0, 127.2, 122.9, 121.3, 119.4, 114.2, 86.4, 82.8, 82.2, 78.1, 54.3, 35.9, 34.1, 31.8, 30.4, 30.3, 23.0, 21.2, 18.8 ppm. HRMS (MALDI, m/z): calcd for $C_{34}H_{43}ClN_2ORu$ $[M - Cl]^+$ 597.2419, found 597.2429.

Compound ***3g***. Yield: 95%. Mp: >300 °C. Anal. Calcd for $C_{24}H_{31}ClN_2ORu$: C, 57.65; H, 6.25; N, 5.60. Found: C, 57.90; H, 5.99; N, 5.53. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 1H, Ar-*H*), 7.07 (s, 1H, Ar-*H*), 7.02 (s, 2H, im-*H*), 7.01 (s, 1H, Ar-*H*), 5.55 (d, 1H, J = 5.66 Hz, *p*-cymene-C*H*), 5.28 (d, 1H, J = 5.53 Hz, *p*-cymene-C*H*), 5.03 (d, 1H, J = 5.66 Hz, *p*-cymene-C*H*), 4.73 (d, 1H, J = 5.56 Hz, *p*-cymene-C*H*), 3.91(s, 1H, NCH_3), 2.14 (m, 1H, C*H*$(CH_3)_2$), 2.00 (s, 3H, Ar-CH_3), 1.25 (s, 9H, C$(CH_3)_3$), 0.89 (d, 3H, J = 6.94 Hz, CH-CH_3), 0.85 (d, 3H, J = 6.80 Hz, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 128.6, 123.2, 122.9, 120.3, 117.1, 115.0, 102.7, 100.8, 87.4, 83.2, 79.8, 79.1, 37.3, 32.9, 30.6, 29.5, 22.2, 19.9, 17.5 ppm. HRMS (MALDI, m/z): calcd for $C_{24}H_{31}ClN_2ORu$ $[M - Cl]^+$ 465.1474, found 465.1480.

Compound ***3h***.[13e] Yield: 94%. ^{1}H NMR ($CDCl_3$): 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-C*H*), 5.42 (d, 1H, J = 5.60 Hz, *p*-cymene-C*H*), 4.90 (d, 1H, J = 5.65 Hz, *p*-cymene-C*H*), 4.56 (d, 1H, J = 5.59 Hz, *p*-cymene-C*H*), 3.90 (s, 3H, NCH_3), 2.16 (m, 1H, C*H*$(CH_3)_2$), 1.97 (s, 3H, Ar-CH_3), 1.50 (s, 9H, C$(CH_3)_3$), 1.25 (s, 9H, C$(CH_3)_3$), 0.94 (d, 3H, J = 6.75 Hz, CHCH_3), 0.82 (d, 3H, J = 6.91 Hz, CHCH_3) ppm.

Crystallographic Studies. Single crystals of **3b** suitable for X-ray diffraction were obtained from CH_3CN/hexane. Data collections were carried out on a Rigaku Saturn 70 diffractometer equipped with a rotating anode system at 113(2) K by using graphite-monochromated Mo Kα radiation (ω−2θ scans, λ = 0.710 73 Å). Data processing followed a similar method to that described in our previous report.[13e]

ROMP of NBE. ROMP of NBE followed a similar procedure to that described in our previous report.[13e]

■ ASSOCIATED CONTENT

Supporting Information

A CIF file for **3b**, figures of NMR spectra for **1a,b**, **2a−h**, and **3a−h**, NMR spectra, and GPC curves for the obtained polymers. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00256.

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Notes

The authors declare no competing financial interest.

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