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Pseudo-Halide and Nitrate Derivatives of Grubbs and Grubbs–Hoveyda Initiators: Some Structural Features Related to the Alternating Ring-Opening Metathesis Copolymerization of Norborn-2-ene with Cyclic Olefins

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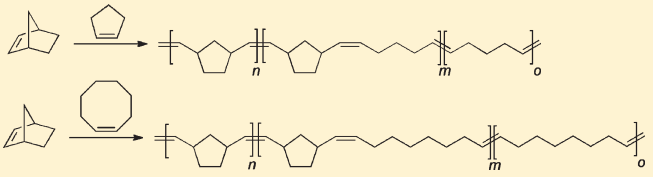
Supporting Information

ABSTRACT: A series of novel Ru–alkylidene-based initiators, in which both chloride ligands were replaced by pseudo-halides or by nitrate, i.e., $[Ru(NCO)_2(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1b**), $[Ru(CF_3SO_3)_2(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1c**), $[Ru(NCO)(CF_3SO_3)(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1d**), $[Ru(CF_3SO_3)(CF_3CO_2)(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1e**), $[Ru(NCS)_2(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1f**), $[Ru(NO_3)_2(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (**2d**), and $[Ru((CF_2)_3(CO_2)_2)(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)(C_6H_4)]$ (**2f**) ($IMesH_2$ = 1,3-dimesitylimidazolin-2-ylidene), have been prepared. The novel initiators and those of the general formula $[RuX_2(L)_n(NHC)(CHPh)]$ and $[RuX_2(NHC)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (X = Cl, C_6F_5COO; NHC = $IMesH_2$, 1,3-dimesitylpyrimidin-2-ylidene, 1,3-dimesityldiazepin-2-ylidene, 1-mesityl-3-(2-phenylethyl)imidazolin-2-ylidene, 1-mesityl-3-adamantylimidiazolin-2-ylidene; L = PCy_3, pyridine, n = 1, 2) were investigated for their propensity to copolymerize NBE with cyclopentene (CPE) and *cis*-cyclooctene (COE), respectively, in an alternating way. Alternating copolymers, that is, poly(NBE-*alt*-CPE)$_n$ and poly(NBE-*alt*-COE)$_n$ containing up to 55 and 40% alternating diads, respectively, were obtained. Moreover, initiator **4b** turned out to be a highly efficient initiator for the homopolymerization of cyclopentene (CPE), allowing for the synthesis of high-molecular-weight poly(CPE). Some fundamental effects of the nature of the pseudo-halide ligand on the extent of alternating copolymerization of NBE with CPE or COE are presented. Finally, the effects of the ring size of the N-heterocyclic carbene on the configuration of the double bonds in the final polymer are addressed.



INTRODUCTION

During the past 20 years, remarkable progress in more efficient and selective metathesis catalysts has been achieved paving the way for various types of metathesis-based reactions in organic and polymer chemistry as well as in materials science.[1] Both well-defined Schrock-[2−5] and Grubbs-type initiators[1,6,7] match well the requirements for ring-opening metathesis polymerization (ROMP)[8,9] and in many cases allow for truly living polymerizations. Significant efforts have been put into the development of even more efficient and active Ru–alkylidene metathesis catalysts. For these purposes, numerous variations in the N-heterocyclic carbene (NHC) as well as in the alkylidene (benzylidene) ligand have been reported.[10] Our group developed modified Grubbs- and Grubbs–Hoveyda initiators by replacing the parent chloride ligands in complexes of the general formula $RuCl_2(L)_n(NHC)(CHR)$ (NHC = $IMesH_2$, 1,3-dimesitylpyrimidin-2-ylidene, 1,3-dimesityldiazepin-2-ylidene, 1-mesityl-3-(2-phenylethyl)imidazolin-2-ylidene; L = PCy_3, pyridine; n = 1, 2; R = Ph, 2-PrO-C_6H_4, $(OMe)_3$-C_6H_2, 2-PrO-5-NO_2-C_6H_3) by pseudo-halide ligands such as triflates, carboxylates, phenoxides, isocyanates, and isothiocyanates.[11−16]

Here, we report on a library of novel Ru–alkylidenes by replacing the chloride ligand by electron-withdrawing pseudo-halide ligands such as isocyanates (OCN^-), isothiocyanates (SCN^-), perfluorocarboxylates (e.g., $CF_3CO_2^-$, $\{(CF_2)_3(CO_2^-)_2\}$), nitrate, and trifluoromethanesulfonates ($CF_3SO_3^-$) (Figure 1).[14,15,17] In some cases we were able to prepare the mono(pyridine)-based "third-generation Grubbs-type" versions instead of the synthetically more easily accessible 2-PrO-benzylidene (Hoveyda-type) versions of these initiators. In total, 23 modified Grubbs- and Grubbs–Hoveyda-type initiators were investigated for their propensity to promote the alternating copolymerization[18−26] of NBE with cyclopentene (CPE) and COE, respectively. Since both the selectivity and reactivity of Grubbs- or Grubbs–Hoveyda-type initiators are governed by the nature of the N-heterocyclic carbene (NHC), of the alkylidene and the anionic (pseudo) halide ligands,[10] one goal of

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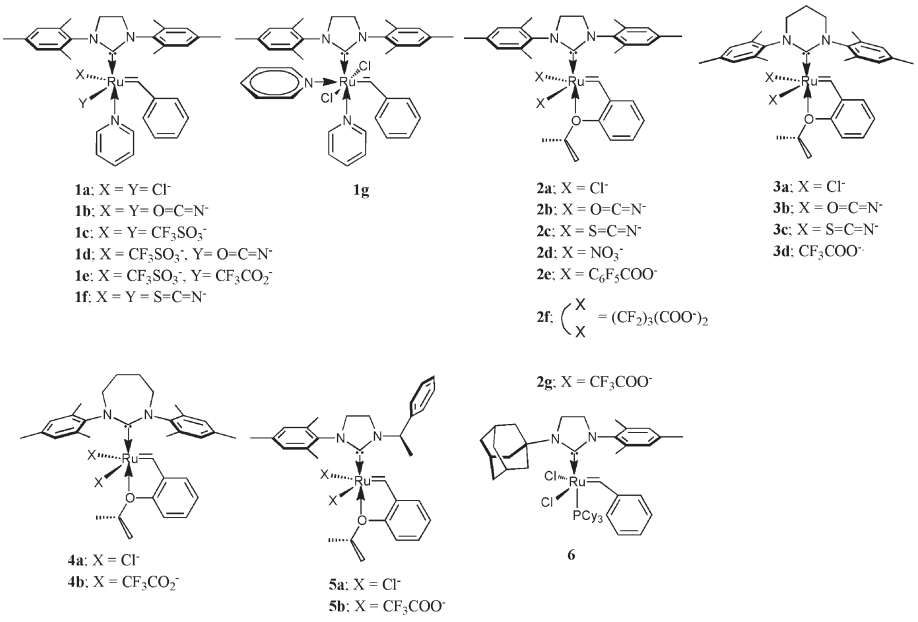

Figure 1. Structure of initiators **1a**−**g**, **2a**−**g**, **3a**−**d**, **4a**,**b**, **5a**,**b**, and **6**.

this investigation was therefore to identify the influence of each of these ligands on the extent of alternating copolymerization.

RESULTS AND DISCUSSION

Synthesis of Initiators. Initiators **1a**−**g**, **2a**−**d**, **3a**−**c**, **4a**,**b**, **5a**,**b**, and **6** (Figure 1) were prepared according to reported procedures.[12,17,27,28]

The modified second-generation Grubbs- and Grubbs−Hoveyda-type initiators $[Ru(NCO)_2(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1b**), $[Ru(CF_3SO_3)_2(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1c**), and $[Ru(NCS)_2(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1f**) were prepared from $[RuCl_2(C_5H_5N)_2(IMesH_2)(CHPh)]$ (**1a**) via reaction with 2 equiv of AgOCN, CF_3SO_3Ag, and AgSCN, respectively. The complex $[Ru(NCO)(CF_3SO_3)(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1d**), which contains two different pseudo-halide ligands, was accessible in a one-pot reaction from **1a** using equimolar amounts of CF_3SO_3Ag/AgOCN and CF_3SO_3Ag/CF_3COOAg, respectively (1 equiv each). Similarly, $[Ru(CF_3SO_3)(CF_3CO_2)(IMesH_2)(C_5H_5N)(CHC_6H_5)]$ (**1e**) was prepared from **1a** and CF_3SO_3Ag/CF_3COOAg (1 equiv each). In view of the excellent leaving group character of the triflate moiety, the high-yield formation of the mixed-ligand initiators **1d** and **1e** is remarkable. In fact, this suggests a high stability of the Ru−triflate bond effectively preventing ligand scrambling as observed, e.g., for the Ru−alkylidenes bearing one chloro and one trifluoroacetate ligand.[29] Consequently, to the best of our knowledge, complexes **1d** and **1e** are, together with the pyridine-free system $[Ru(CF_3SO_3)(CF_3CO_2)(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4)]$[12] and a chiral catalyst reported by the Hoveyda group, which links the NHC via a chiral binaphth-1-olate to the Ru,[30,31] the so far only existing stable Ru−alkylidenes bearing two different anionic ligands. As one might expect, the ^{19}F NMR of **1c** shows one signal for the 2 equiv CF_3SO_3 groups at δ = −78.81 ppm, while the one for **1e** shows two signals at δ = −76.94 ppm (CF_3COO) and −78.95 ppm (CF_3SO_3), further confirming the mixed ligand structure.

$[Ru(NO_3)_2(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (**2d**) was prepared from $RuCl_2(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)$ and 2 equiv of $AgNO_3$ in THF and is to the best of our knowledge the first Ru−alkylidene−dinitrate complex. It was isolated as a brown solid in 84% yield. In the ^1H NMR spectrum, a significant downfield shift of the signal for the alkylidene proton (δ = 18.63 ppm) as compared to the parent second-generation Grubbs−Hoveyda initiator (δ = 16.56 ppm)[32] was observed, which is indicative for a stronger ionic character of the Ru−NO_3 bonds as compared to the Ru−Cl bonds, ultimately resulting in a stronger polarization of the Ru−alkylidene bond. Finally, $[Ru((CF_2)_3(CO_2)_2)(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)(C_6H_4)]$ (**2f**) was prepared from $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ via reaction with 1 equiv of the disilver salt of hexafluoroglutaric acid $[(CF_2)_3(CO_2Ag)_2]$ and isolated as a red-brown solid in 86% yield. In the ^1H NMR spectrum, **2f** was characterized by a downfield shift of the alkylidene proton signal to δ = 17.34 ppm and is one of the very rare examples of a ruthenium−alkylidene bearing a chelating X_2 ligand.[33]

ROMP of Norborn-2-ene (NBE) and *cis*-Cyclooctene (COE). Compounds **1a**−**g**, **2a**−**g**, **3a**−**d**, **4a**,**b**, **5a**,**b**, and **6** are active initiators for the ROMP of NBE.[12,17,27,28] Poly(NBE) was prepared applying an NBE:initiator ratio of 1000:1 (Table S1, Supporting Information). In no case, a truly living polymerization was observed as indicated by the polydispersity indices (PDIs), which were monomodal, however, in the range of 1.2 < PDI < 4.1 and the differences between the theoretical and experimentally determined values for M_n. Interestingly, the observed cis-content was around 50% for most initiators, except for initiator **1f** bearing two isothiocyanate ligands (σ_{cis} = 70%) and for initiators based on a 7-membered NHC (i.e., **4a**, **4b**, σ_{cis} = 75%). Such a high cis-selectivity is unprecedented for Ru−alkylidenes bearing symmetrically substituted NHC and has only been realized with the aid of Ru−alkylidenes bearing chelating phosphines.[23] In terms of initiator activity, the pyridine-containing initiators **1b**, **1d**, **1e**, and **1g** as well as the pyridine-free, perfluorocarboxylate-, nitrate-, and isocyanate-based systems **2b**, **2d**−**f**, **3b**, **4b**, and **5b** but also **4a** need to be mentioned. Thus, at room temperature, the ROMP of NBE was completed in 5−50 s using 0.1 mol % of initiator with respect to NBE (Table S1, Supporting Information). In contrast, the isothiocyanate-based initiators **1f**, **2c**, and **3c** as well as the bis(trifluoromethanesulfonate)-based **1c** showed a comparable

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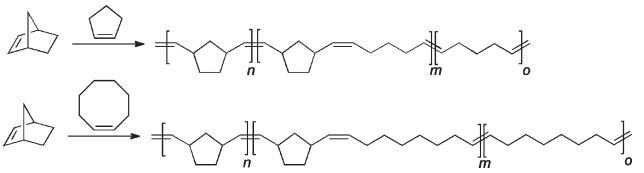
Scheme 1. Alternating Copolymerization of NBE with CPE and COE, Respectively



moderate reactivity in the ROMP of NBE. There, applying the same conditions, monomer consumption required up to 45 min. To explain for these findings, one might think of some bimolecular interactions between the thiophilic Ru and the isothiocyanate; however, this remains speculative.

The results for the homopolymerization of COE are summarized in Table S2. Similar to the homopolymerization of NBE, no living polymerization character could be identified with any of the initiators. However, because of the pronounced propensity of poly(COE) to undergo backbiting via secondary metathesis, thereby changing both the PDI and M_n values of the polymers, the results for the homopolymerization of COE in terms of PDI and M_n must be treated carefully and should not be overinterpreted.

Alternating Copolymerization of Norborn-2-ene (NBE) with Cyclopentene (CPE). Next, we used initiators **1a**−**e**, **2a**−**g**, **3a**−**d**, **4a**,**b**, **5a**,**b**, and **6** in the copolymerization of NBE with CPE using a NBE:CPE ratio of 1:1 (Scheme 1).

Because of its bicyclic nature, NBE is a by far more reactive monomer in ROMP than cyclopentene. Consequently, usually a considerable excess of CPE is used in the copolymerization with NBE in order to realize a substantial fraction of alternating diads in the corresponding copolymer.

Despite the low NBE:CPE ratio used here, the resulting copolymers contained up to 55% alternating diads (initiator **5a**, entry 19, Table 1), which is indicative for steric constraints in the NBE homopolymerization and which can be avoided by an alternating insertion of CPE. The number-average molecular weights were in the range of 3000 < M_n < 140 000 g/mol, again indicative for a nonliving polymerization conditions. All copolymers obtained had a monomodal distribution with PDIs typically in the range of 1.5−2.5 (data not shown). Despite the higher PDIs, the presence of three individual polymers, i.e., poly(NBE), poly(CPE), and an alternating copolymer, was excluded by using different NBE:CPE ratios, resulting in different fractions of both the poly(NBE) and poly(CPE) homopolymer blocks in the copolymer. There, the presence of either low- or high-molecular-weight poly(NBE) or poly(CPE) homopolymers instead of small/large poly(NBE) or poly(CPE) blocks in the copolymer would have resulted in at least bimodal distributions. Furthermore, there is no chemical reason why the same initiator should make alternating copolymers on the one hand and pure homopolymers on the other at the same time. A representative ^{13}C NMR of a copolymer prepared by the action of **4b** is shown in Figure 2.

There, the signals for poly(NBE) at δ = 133−134 ppm can be detected.[24,25] The signals around δ = 130 ppm stem from the poly(CPE) block. The signals around δ = 135−136 and 128−129 ppm can be clearly attributed to the alternating copolymer. The first set of signals around δ = 135−136 ppm is designated to the C═C−CH_2 carbon atoms and consists of eight different signals at 135.64, 135.55, 135.41, 135.33, 135.18, 135.05, 134.99, and 134.91 ppm, which can be attributed to the corresponding ccc, tcc, ctc, cct, ttc, tct, ctt, and ttt diads.[18,19] The less resolved signals around δ = 128−129 ppm are assigned to the C═C−CH_2 carbon atoms and correspond to the same diads.

Table 1. Alternating Copolymerization of NBE and CPE by the Action of Initiators 1a−e, 2a−g, 3a−d, 4a,b, 5a,b, and 6[a]

		poly(NBE)		poly(CPE)		poly(NBE-*alt*-CPE)$_n$
no.	initiator	(%)	cis/trans	(%)	cis/trans	(%)
1	**1a**	78	50/50	7	30/70	15
2	**1b**	88	60/40	4	20/80	8
3	**1c**	91	60/40	2	n.a.	7
4	**1d**	85	60/40	5	30/70	10
5	**1e**	66	60/40	8	30/70	26
6	**2a**	65	40/60	20	15/85	15
7	**2b**	66	60/40	17	20/80	17
8	**2c**	90	60/40	3	30/70	7
9	**2d**	64	40/60	5	20/80	31
10	**2e**	57	70/30	11	20/80	32
11	**2f**	78	60/40	6	30/70	16
12	**2g**	48	40/60	22	30/70	30
13	**3a**	85	70/30	10	15/85	5
14	**3b**	86	50/50	5	20/80	9
15	**3c**	89	50/50	2	25/75	9
16	**3d**	50	60/40	13	15/85	37
17	**4a**	77	75/25	10	20/80	13
18	**4b**	50	70/30	10	20/80	40
19	**5a**	29	60/40	16	25/75	55
20	**5b**	59	60/40	24	20/80	17
21	**6**	91	30/70	0		9

[a] Calculated from the ^{13}C NMR spectra, initiator:NBE:CPE = 1:1000:1000, CH_2Cl_2. n.a. = not analyzed because of insufficient signal intensities and/or resolution.

Using a 1:1 ratio of NBE:CPE, the highest content of alternating copolymer with 26−55% of alternating diads was observed with initiators **1e**, **2d**, **2e**, **2g**, **4b**, **3d**, and **5a** (Table 1). The percentage of alternating NBE/CPE diads is also reflected in the copolymerization parameters r_1 *and* r_2 that can be calculated from the ^{13}C NMR spectra applying a first-order Markov model, which ultimately leads to the Mayo−Lewis equation.[34] There, $r_1 = ([1/P_{12}] - 1)([CPE]/[NBE])$ and $r_2 = ([1/P_{21}] - 1)([NBE]/[CPE])$, where P_{12} and P_{21} are the reactivity probabilities for CPE to insert into a growing chain with a terminating NBE and vice versa. In this model, a low conversion (<5%) is a prerequisite for the determination of the copolymerization parameters. Since the polymerization reactions described here are comparable fast, the copolymerization parameters r_1 and r_2 can only be estimated and varied between 1 (**4b**) and 13 (**2c**) for NBE and between 0.1 (**2d**) and 70 (**1b**) for CPE (Table S3, Supporting Information), suggesting a pronounced propensity of most initiators to homopolymerize NBE. Surprisingly, **4b** was found to be an efficient initiator for the homopolymerization of CPE. Thus, 5000 mol equiv of CPE with respect to **4b** was quantitatively consumed within 30 s, yielding poly(CPE) with an M_n of 125 000 g/mol and a PDI of 1.62 (σ_{cis} = 17%).

An important finding that becomes evident is that the use of initiators in which both chlorides have been substituted by electron-withdrawing, potentially chelating ligands such as CF_3COO^-, $CF_3SO_3^-$, NO_3^-, or $C_6F_5COO^-$ as found in **1e**, **2d**, **2e**, **2g**, **3d**, and **4b** favors the formation of alternating

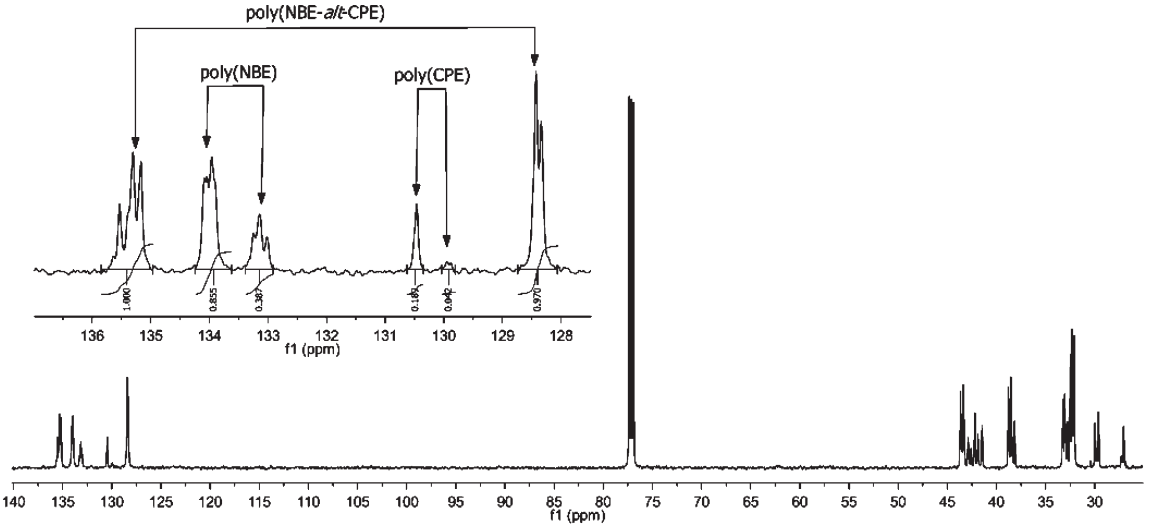


Figure 2. ^{13}C NMR spectrum ($CDCl_3$) of poly(NBE-*alt*-CPE)$_n$ prepared by the action of **4b**.

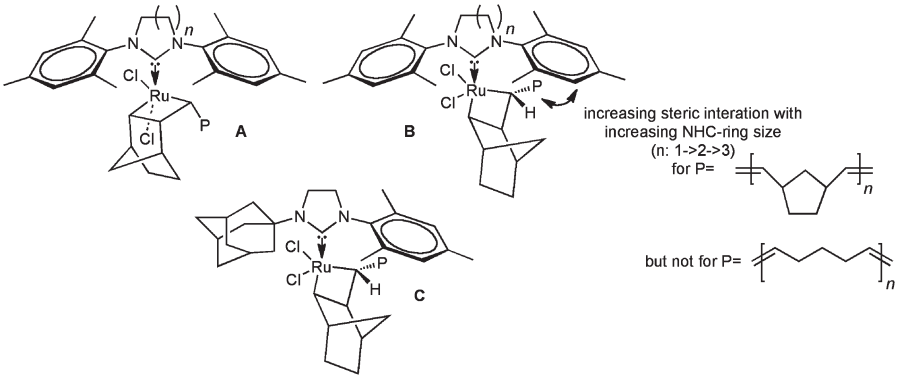


Figure 3. Different ruthenacyclobutanes and impact on the cis/trans configuration of the final polymer.

copolymers. Exceptions are initiator **5a**, which represents an unsymmetrically substituted NHC, as well as **1c** bearing two $CF_3SO_3^-$ ligands. The mechanism of alternating copolymerization with Ru−carbenes bearing unsymmetrically substituted NHCs as realized in **5a** has already been proposed.[24,25,35] The low copolymerization propensity of **1c** is not surprising, since bis(trifluoromethanesulfonate)-substituted metathesis initiators and catalysts often display a reactivity that differs significantly from the one of other anionic ligands and which rather stems from the special features of the $CF_3SO_3^-$ group than from the excellent leaving group character of the ligand. Thus, bis-(trifluoromethanesulfonate)-substituted Mo−alkylidenes are virtually inactive in ROMP, too.[36] Unlike in Mo-based Schrock initiators,[36] no correlation of the electron-withdrawing character of the X ligand with the cis/trans ratio of the final polymer was found.

Cis/Trans Ratios of the Poly(NBE) Homopolymer Blocks in Poly(NBE)-*alt*-Poly(CPE). In the ^1H and ^{13}C NMR spectroscopy, the signals of the cis- and trans-double bonds of poly(NBE)-*alt*-poly(CPE) can be found at δ = 5.38/5.28 and 135.4/128.4 ppm, respectively (Figure S1, Supporting Information). Because of overlapping signals, the cis-content of the alternating diads was hard to determine exactly; however, it was estimated to lie in the range of 50 < σ_{cis} < 70% throughout. Except for initiators **2e**, **3a**, **4a**, **4b**, and **6**, a cis:trans ratio around 1:1 was observed for the poly(NBE) block. A comparison of initiators **1a**, **2a**, **3a**, and **4a**, which differ in the size of the NHC (i.e., imidazolin-2-ylidene (**1a**, **2a**) vs pyrimidin-2-ylidene (**3a**) or 1,3-diazepin-2-ylidene (**4a**), reveals no differences in their propensity to produce alternating copolymers from NBE with CPE (Table 1). However, changing from the imidazolin-2-ylidene (**1a**) to the pyrimidin-2-ylidene (**3a**) and 1,3-diazepin-2-ylidene (**4a**) results in a strong increase of the cis-content in homopoly(NBE) (50/50 → 70/30 → 75/25, Table 1). The high cis-content of the poly(NBE) homopolymer blocks apparently origins from NHCs based on tetrahydropyrimidin-2-ylidenes and diazepin-2-ylidenes. In these NHCs, the angle at the nitrogens defined by the mesityl group and the carbene are smaller than those on imidazolin-2-ylidenes; consequently, the two mesityl groups are located closer to the Ru−alkylidene than in **1a**. In due consequence, the steric interaction between the growing polymer chain (P) and the mesityl groups increases in case an intermediary ruthenacyclobutane trans to the NHC forms (structure B, Figure 3). As an alternative, a ruthenacyclobutane with side-on coordination and one Cl ligand trans to the NHC can be proposed (structure A, Figure 3). In order to reduce the steric interaction between the growing polymer chain and mesityl groups, a cis-configured ruthenacyclobutane is favored, which gives raise to cis-configured double bonds along the polymer chain (Figure 3).

In contrast, the use of initiator **6** bearing the unsymmetrically substituted NHC results in the formation of poly(NBE) blocks

Table 2. Alternating Copolymerization of NBE and CPE by the Action of Initiators 2d, 4b, and 6 Using Different Monomer Ratios (Solvent = CH_2Cl_2, T = 25 °C, t = 3 min)[a]

		poly(NBE)		poly(CPE)		poly(NBE-*alt*-CPE)$_n$
initiator	I:NBE:CPE	(%)	cis/trans	(%)	cis/trans	(%)
2d	1:1000:1000	64	40/60	5	20/80	31
2d	1:1000:5000	28	30/70	26	30/70	46
2d	1:1000:7000	22	30/70	35	30/70	43
2d	1:1000:10000	11	30/70	50	30/70	39
2d	1:1000:50000	0		73	30/70	27
4b	1:1000:500	68	70/30	3	0/100	29
4b	1:1000:1000	50	70/30	10	20/80	40
4b	1:1000:2000	18	70/30	47	20/80	35
6	1:1000:1000	91	30/70	0		9
6	1:1000:3000	81	30/70	0		19
6	1:1000:4000	74	30/70	0		26
6	1:1000:10000	58	20/80	0		42
6	1:1000:20000	51	10/90	5	11/89	44
6	1:1000:30000	42	20/80	11	12/88	47
6	1:1000:40 000	33	10/90	16	10/90	51
6	1:1000:50000	28	15/85	19	14/86	53
6	1:1000:60000	14	10/90	38	13/87	48

[a] Calculated from the ^{13}C NMR spectra, reaction time 2 min, CH_2Cl_2.

with a high trans-content (70%). This particular feature of **6** is most probably elated to the restricted rotation of the NHC ligand around the Ru−C_2 bond, thereby forcing the propagating alkylidene to remain at the same side as the mesityl ligand.[28] There, a ruthenacyclobutane trans to the NHC is energetically favored (structure C, Figure 3), resulting in a higher fraction of trans-configured double bonds in the polymer. As outlined for the alternating copolymerization of NBE with CPE by the action of **5a**, poly(CPE)-derived Ru−alkylidenes are sterically much less demanding than poly(NBE)-derived Ru−alkylidenes. Consequently, ruthenacyclobutanes trans to the NHC should dominate, giving raise to larger fractions of trans-configured double bonds in the poly(CPE) blocks. In fact, these poly(CPE) blocks were characterized by a cis:trans ratio around 20:80 throughout.

Despite the correlations outlined above, one has to state that the influence of changes in both the NHC and the X-ligand on both the initiator's reactivity and the polymer structure are much less pronounced than, e.g., in Schrock-type carbenes. This is attributed to the nature of the Ru=C bond, which is, as confirmed by numerous electrochemical measurements,[1,37] more a Ru(II)−carbene than a true Ru(IV)−alkylidene, which is in stark contrast to high-oxidation-state Schrock catalysts,[3,5,38] which possess a pronounced metal−alkylidene character.

Influence of the NBE:CPE Ratio on the Extent of Alternating Copolymerization. To further explore the scope and limits of the alternating copolymerization of NBE with CPE, we focused on the most promising initiators, i.e., **2d**, **4b**, and **6**, and used different NBE:CPE ratios. The results in terms of the percentage of alternating diads are summarized in Table 2. With **2d**, an increase in the NBE:CPE ratio from 1:1 to 1:5 resulted in an increase in the content of the alternating diads from 31 to 46% (Table 2, Figure S2, Supporting Information).

A further increase of the NBE:CPE ratio up to 1:50, however, resulted in a decrease in the content of alternating diads and, concomitantly, in a strong decrease in the formation of the poly(NBE) homopolymer block as well as in a significant increase in the formation of the poly(CPE) homopolymer block. Similar results were found for initiators **4b**. There a maximum of alternating diads of 40% was found (Table 2). These data clearly show that, irrespective of the anionic ligand, the NHC, and the NBE:CPE ratio used, the content of alternating diads was <53% throughout for initiators **2d** and **4b** and thus much smaller than in alternating copolymers prepared by the action of unsymmetrical NHC ligands.[24,25] To clarify the role of such unsymmetrical NHCs, we also investigated the scope and limitations of a Grubbs-type initiator bearing such an unsymmetrically substituted N-heterocyclic carbene (NHC), i.e., [$RuCl_2$(IAdMesH_2)-(CHPh)(PCy_3)] (**6**) containing one (comparably small) mesityl and one (large) adamantyl group in the 1- and 3-position of the imidazolin-2-ylidene, respectively. Using different ratios of NBE:CPE (1:1 to 1:50), the percentage of alternating diads could in fact be increased from 9 to 53% (Table 2, Figure S3, Supporting Information).

Table 3. Alternating Copolymerization of NBE and COE by the Action of Initiators 1a−e, 2a−g, 3a−d, 4a,b, 5a,b, and 6[a]

		poly(NBE)		poly(COE)		poly(NBE-*alt*-COE)$_n$
no.	initiator	(%)	cis/trans	(%)	cis/trans	(%)
1	**1a**	42	60/40	48	20/80	10
2	**1b**	42	60/40	44	30/70	14
3	**1c**	100	60/40	0		0
4	**1d**	67	60/40	27	60/40	6
5	**1e**	79	40/60	13	30/70	8
6	**2a**	65	70/30	20	20/80	15
7	**2b**	39	40/60	44	20/80	17
8	**2c**	59	60/40	29	40/60	12
9	**2d**	70	40/60	18	50/50	12
10	**2e**	77	70/30	15	30/70	8
11	**2g**	47	40/60	45	25/75	8
12	**3a**	36	70/30	64	30/70	0
13	**3b**	42	60/40	50	20/80	8
14	**3c**	46	50/50	32	45/55	22
15	**3d**	100	50/50	0		0
16	**4a**	49	70/30	48	30/70	3
17	**4b**	99	80/20	1		0
18	**5a**	29	60/40	31	40/60	40
19	**5b**	53	60/40	38	40/60	9
20	**6**	88	20/80	8	10/90	4

[a] Calculated from the ^{13}C NMR spectra, initiator:NBE:COE = 1:1000:1000, CH_2Cl_2.

Alternating Copolymerization of NBE with *cis*-Cyclooctene (COE). We also briefly looked into the copolymerization of NBE with COE,[21−23] again using a NBE:COE ratio of 1:1 (Scheme 1). The results are summarized in Table 3.

Initiators **1c** and **4b** bearing $CF_3SO_3^-$ and CF_3COO^- groups, respectively, produced only poly(NBE) under the given conditions. Among all initiators investigated, **3c** showed the highest, though still quite modest content of 22% of alternating diads. Generally, with all initiators the percentage of alternating units obtained in the copolymerization of NBE with COE is lower than in the copolymerization of NBE with CPE (Table 1). A representative ^{13}C NMR is shown in Figure 4.

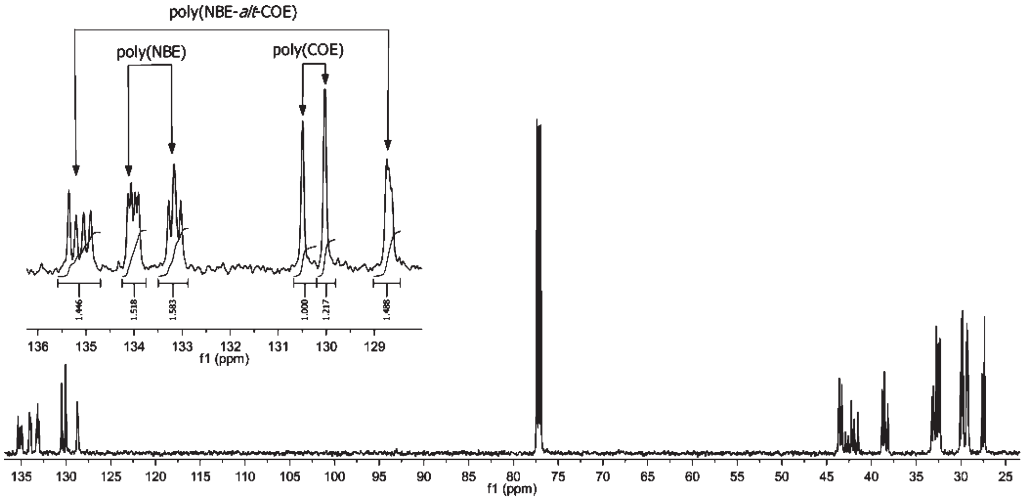


Figure 4. ^{13}C NMR spectrum ($CDCl_3$) of poly(NBE-alt-COE)$_n$ prepared by the action of **3c**.

As for the copolymerization of NBE with COE, a cis-content in the alternating copolymer around 50% was estimated. The estimated copolymerization parameters r_1 and r_2 varied between 2 (**2b**, **3c**) and 19 (**6**) for NBE and between 2 (**1e**, **2d**, **2e**, **3c**) and 19 (**4a**) for COE (Table S4, Supporting Information), indicating a strong propensity for the homopolymerization of both NBE and COE for all initiators.

Polymerization Kinetics. Finally, selected kinetic studies were performed. Two initiators that allow for a higher alternating copolymer content, i.e., **2d** and **4b**, as well as two initiators with a lower propensity to copolymerize NBE and CPE in an alternating way (**1e**, **6**) were chosen. The homopolymerization of NBE as well as the copolymerizations of NBE with CPE and COE with initiators **1e**, **2d**, **4b**, and **6** followed first-order kinetics in NBE (Figures S4−S24, Supporting Information). The rate constants (k_p) for the homopolymerization of NBE by the action of **1e, 2d**, **4b**, and **6** were 5.6, 5.6, 1.8, and 15.5 s^{-1}, respectively, while the rate constants of polymerization of NBE in the copolymerization with CPE were 3.5, 9.5, 4.7, and 2.1 s^{-1}, respectively, and thus within the same order of magnitude (Supporting Information). In other words, in the copolymerization with CPE a slight increase in k_{pNBE} was observed for **2d** and **4b** and correlates with the higher fraction of alternating diads in the copolymer (31 and 40%, Table 1). Vice versa, a decrease in k_{pNBE} was observed for **1e** and, even more pronounced, for **6**, for which 26 and 9% of alternating diads were found (Table 1). The same accounts for the copolymerization of NBE with COE. In this copolymerization, the rate constants (k_p) for NBE with **1e**, **4b**, and **6** were 2.3, 2.0, and 11 s^{-1} (Figures S16, S21, and S24, Supporting Information) and thus lower than the values for k_{pNBE} in homopolymerization. Again, the low degrees of copolymerization (8, 0, and 4%, Table 3) account for these findings.

SUMMARY

A series of modified second-generation Grubbs- and Grubbs−Hoveyda-type metathesis initiators in which the chloride ligand was replaced by electron-withdrawing pseudo-halide ligands have been investigated for their ROMP activity vs NBE as well as for their propensity to copolymerize NBE with cyclic olefins such as COE and CPE. Ru$(CF_3COO)_2$(1,3-dimesityl-1,3-diazepinidin-2-ylidene)(CH-2-(2-PrO)-C_6H_4) (**4b**) was identified as an unusually active initiator for the homopolymerization of cyclopentene. All initiators containing electron-withdrawing ligands, potentially chelating showed high activity in the alternating copolymerization with NBE/CPE. In addition, in the copolymerization with CPE, an increase in the size of the NHC favors the formation of poly(NBE) blocks with a high cis-content.

EXPERIMENTAL SECTION

General. All manipulations were performed under an N_2 atmosphere in a glovebox (LabMaster 130, MBraun, Garching, Germany). Pentane, toluene, and CH_2Cl_2 were dried by using a solvent purification system (SPS, MBraun). Pyridine, *cis*-cyclooctene (COE), cyclopentene (CPE), and 1,5-cyclooctadiene (COD) were dried over CaH_2 and distilled under Ar. Benzene was distilled from sodium benzophenone under nitrogen. $CDCl_3$ and CD_2Cl_2 were distilled from CaH_2 and stored over molecular sieves (4 Å). Purchased starting materials and other chemicals or reagents (Aldrich, Fluka) were used without further purification.

NMR spectra were recorded on a Bruker Avence 600 spectrometer (600.25 MHz for proton and 150.93 MHz for carbon spectra) at room temperature. High-resolution mass spectra (ESI) were recorded on an APEX II FTICR mass spectrometer (Bruker Daltonics). Infrared spectra were recorded from 4000 to 400 cm^{-1} on a Perkin-Elmer 881 spectrometer using ATR technology. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050 equipped with an AOC-20i autosampler using an SPB fused silica (Rxi-5MS) column (30 m × 0.25 mm × 0.25 μm film thickness) and on a Shimadzu GCMS-QP2010S equipped with an AOC-20i autosampler using a SPB fused silica (Rxi-5MS) column (30 m × 0.25 mm × 0.25 μm film thickness). The injection temperature was 150 °C; the initial column temperature was 40 °C and was then increased to 120 °C within 7 min. GPC measurements were performed on an LC10 AD liquid chromatograph equipped with an SIL-10 ADVP autoinjector, a CTO-10AC column oven, an SCL-10AVP system controller, and an RID-10A refractive index detector (all Shimadzu). A precolumn and three consecutive PLgel 5 μm MiniMIX-c columns (7.5 × 300 mm, Polymer Laboratories) were operated in $CHCl_3$ applying a flow rate of 0.3 mL/min. Alternatively, GPC measurements were carried out in $CHCl_3$ at 30 °C on a GPC system consisting of a Waters 515 HPLC pump, a Waters 717 plus autosampler, and a Waters 2414 RI index and a Waters 2489 UV detector using three consecutive Waters styragel HR4 columns (4.6 × 300 mm) operated at a flow rate of 1 mL/min. Poly(styrene) standards 400 < M_n < 2000 000 g/mol were used for

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calibration. The syntheses of **1a**,[39,40] **1g**,[41] **2a**,[32] **2b**,[15] **2c**,[15] **2e**,[14] **3a**−**3c**,[15] **4a**, **4b**[17] **5a**, **5b**,[14] and **6**[28] are described elsewhere.

[Ru(NCO)$_2$(IMesH$_2$)(C$_5$H$_5$N)(CHC$_6$H$_5$)] (1b). **1a** (150 mg, 0.21 mmol) was dissolved in benzene (10 mL), and a solution of AgOCN (66 mg, 0.44 mmol) in benzene (2 mL) was slowly added to the stirred solution. Stirring at room temperature was continued for another 2 h. The chloride exchange was accompanied by a color change to dark green. The solvent was removed *in vacuo*, the resulting material was redissolved in CH_2Cl_2 and filtered through Celite, and then the filtrate was dried. The residue was washed with pentane (3 × 15 mL) and recrystallized from CH_2Cl_2/pentane at −50 °C, yielding a green solid in 88% yield (120 mg, 0.18 mmol). ^{1}H NMR (CD_2Cl_2): δ = 18.47 (s, 1H, RuC*H*), 8.53 (bs, 2H, py, *o*-C*H*), 7.69 (bs, 1H, py, *p*-C*H*), 7.52 (d, J_{H-H} = 6.0 Hz, 2H, Ph, *o*-C*H*), 7.45 (t, J_{H-H} = 7.8 Hz, 1H, Ph, *p*-C*H*), 7.09 (t, J_{H-H} = 7.8 Hz, 4H, Ph, *m*-C*H*; py, *m*-C*H*), 6.78 (s, 4H, Ar, Mes-C*H*), 4.01 (s, 4H, CH_2CH_2), 2.38 (s, 12H, Mes-CH_3), 2.20 (s, 6H, Mes-CH_3). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ = 316.5 (m, Ru=CHPh), 216.7 (s, NCN), 151.7, 150.2, 139.1, 138.5, 137.3, 136.8, 135.9, 130.5, 130.0, 129.9, 128.9, 126.9, 124.0, 123.7, 123.3, 53.5, 53.0, 21.2, 18.4. FT-IR (ATR mode): 3528 (w), 2914 (w), 2227 (vs), 1602 (m), 1483 (m), 1446 (m), 1407 (w), 1314 (m), 1265 (m), 1070 (w), 1037 (w), 851 (w), 759 (w), and 697 (m), 637 cm^{-1} (m). HRMS (ESI) calcd for $C_{33}H_{37}N_5O_2Ru$: 661.199 07; found: 661.208 95 $[M]^{\bullet+}$.

[Ru(CF$_3$SO$_3$)$_2$(IMesH$_2$)(C$_5$H$_5$N)(CHC$_6$H$_5$)] (1c). **1a** was dissolved in benzene (10 mL), and a solution of CF_3SO_3Ag (113 mg, 0.44 mmol) in benzene (2 mL) was slowly added. The mixture was stirred at room temperature for 2 h; complete chloride exchange was accompanied by a color change from green to dark brown. The solvent was evaporated to dryness, the residue was dissolved in CH_2Cl_2 and filtered through Celite, and then the filtrate concentrated to dryness. The material was washed with pentane (3 × 15 mL) and dried. Recrystallization from CH_2Cl_2/pentane at −50 °C afforded a brown solid in 89% yield (160 mg, 0.18 mmol). ^{1}H NMR (CD_2Cl_2): δ = 18.98 (s, 1H, RuC*H*), 8.57 (bs, 2H, py, *o*-C*H*), 7.88−7.86 (m, 1H, py, *p*-C*H*), 7.72 (bs, 2H, Ph, *o*-C*H*), 7.40−7.35 (m, 1H, Ph, *p*-C*H*), 7.22 (bs, 4H, Ph, *m*-C*H*; py, *m*-C*H*), 6.99 (s, 4H, Ar, Mes-C*H*), 4.05 (s, 4H, CH_2CH_2), 2.36 (s, 6H, Mes-CH_3), 1.94 (s, 12H, Mes-CH_3). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ = 333.8 (m, Ru=CHPh), 211.3 (s, NCN), 156.7, 156.3, 152.1, 150.1, 141.4, 139.5, 137.2, 135.5, 134.9, 130.4, 129.7, 128.8, 127.1, 126.7, 126.1, 52.5, 51.2, 21.5, 19.1. ^{19}F NMR (CD_2Cl_2, 564.8 MHz): δ = −78.81. FT-IR (ATR mode): 3538 (w), 2922 (w), 1605 (m), 1486 (m), 1447 (m), 1260 (vs), 1223 (m),1157 (m), 1068 (w), 1029 (s), 858 (w), 802 (w), 760 (m), 702 (m), 637 cm^{-1} (m). HRMS (ESI) calcd for $C_{35}H_{37}F_6N_3O_6S_2Ru^+$: 875.1071; found: 726.157 $[M-CF_3SO_3]^+$.

[Ru(NCO)(CF$_3$SO$_3$)(IMesH$_2$)(C$_5$H$_5$N)(CHC$_6$H$_5$)] (1d). **1a** (150 mg, 0.21 mmol) was dissolved in benzene (10 mL), and a suspension of CF_3SO_3Ag (56.7 mg, 0.22 mmol) and AgOCN (33 mg, 0.22 mmol) in benzene (2 mL) was slowly added to the stirred solution. Stirring at room temperature was continued for another 2 h, and a color change to dark green was observed. The solvent was evaporated to dryness, the remaining material was redissolved in CH_2Cl_2 and filtered through Celite, and then the solvent was removed *in vacuo*. The residue was washed with pentane (3 × 15 mL) and dried. The crude product was recrystallized from CH_2Cl_2/pentane at −50 °C, affording a green solid in 80% yield (127 mg, 0.17 mmol). ^{1}H NMR (CD_2Cl_2): δ = 17.85 (s, 1H, RuC*H*), 7.87−7.83 (m, 1H, py, *o*-C*H*), 7.78−7.76 (m, 1H, py, *o*-C*H*), 7.65 (t, 1H, J_{H-H} = 7.2 Hz, py, *p*-C*H*), 7.57 (bs, 2H, Ph, *o*-C*H*), 7.39 (bs, 1H, Ph, *p*-C*H*), 7.33−7.26 (m, 4H, py, *m*-C*H*, Ph, *m*-C*H*), 7.23−7.18 (m, 4H, Ar, Mes-C*H*), 4.13 (bs, 2H, CH_2), 4.01 (bs, 2H, CH_2), 2.63 (s, 6H, Mes-CH_3), 2.22 (s, 6H, Mes-CH_3), 1.63 (s, 6H, Mes-CH_3). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ = 324.8 (m, Ru=*C*HPh), 210.6 (NCN), 154.9, 151.7, 151.6, 151.1, 139.5, 139.1, 137.2, 134.1, 133.4, 130.9, 130.8, 130.5, 129.7, 129.1, 126.6, 126.4, 122.5, 52.1, 21.3, 19.2, 17.3. ^{19}F NMR (CD_2Cl_2, 564.8 MHz): δ = −78.89. FT-IR (ATR mode): 3546 (w), 2919 (w), 2361 (w), 2340 (w), 2235 (vs), 1955 (w), 1604 (m), 1485 (m), 1446 (m), 1261 (s), 1223 (m), 1153 (m), 1070 (w), 1030 (s), 854 (m), 761 (m), 699 (m), 637 cm^{-1} (m). HRMS (ESI) calcd for $C_{35}H_{37}F_3N_4O_4SRu$: 768.153 11; found: 540.160 $[M-CF_3SO_3, -Py]^+$.

[Ru(CF$_3$SO$_3$)(CF$_3$CO$_2$)(IMesH$_2$)(C$_5$H$_5$N)(CHC$_6$H$_5$)] (1e). **1a** (200 mg, 0.28 mmol) was dissolved in benzene (12 mL), and a mixture of CF_3SO_3Ag (74.3 mg, 0.29 mmol) and CF_3COOAg (63.8 mg, 0.29 mmol) in benzene (2 mL) was slowly added to the stirred solution. Stirring at room temperature was continued for another 2 h, and a color change from green to dark brown was observed. The solvent was removed *in vacuo*, and the remaining material was redissolved in CH_2Cl_2 and filtered through Celite. Then, the filtrate was dried. The residue was washed with pentane (3 × 15 mL) and dried. The crude product was recrystallized from CH_2Cl_2/pentane at −50 °C, affording a brown solid in 78% yield (181 mg, 0.22 mmol). ^{1}H NMR (CD_2Cl_2): δ = 18.09 (s, 1H, RuC*H*), 8.67−8.66 (m, 1H, py, *o*-C*H*), 8.55 (t, 1H, J_{H-H} = 7.2 Hz, py, *o*-C*H*), 7.99 (t, 1H, J_{H-H} = 6.6 Hz, py, *p*-C*H*), 7.78−7.75 (m, 2H, Ph, *o*-C*H*), 7.71−7.67 (bs, 1H, Ph, *p*-C*H*), 7.31−7.26 (m, 4H, py, *m*-C*H*, Ph, *m*-C*H*), 7.16−7.13 (m, 4H, Ar, Mes-C*H*), 4.15 (s, 4H, CH_2CH_2), 2.37 (s, 6H, Mes-CH_3), 1.97 (s, 12H, Mes-CH_3). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ = 333.4 (m, Ru=CHPh), 212.5 (NCN), 155.4, 167.8, 155.4, 152.3, 152.2, 140.0, 138.7, 137.3, 135.8, 134.0, 130.5, 129.9, 128.8, 128.1, 126.6, 125.8, 125.7, 124.8, 115.7, 113.8, 53.6, 52.4, 21.2, 18.7. ^{19}F NMR (CD_2Cl_2, 564.8 MHz): δ = −76.94, −78.95. FT-IR (ATR mode): 3525 (w), 2920 (w), 1966 (m), 1671 (m), 1634 (m), 1606 (m), 1486 (m), 1448 (m), 1414 (m), 1264 (vs), 1199 (s), 1152 (s), 1030 (m), 857 (m), 761 (m), 731 (m), 700 (m), and 637 cm^{-1} (m). HRMS (ESI) calcd for $C_{36}H_{37}F_6N_3O_5SRu$: 839.140; found: 690.192 $[M-CF_3SO_3]^+$.

[Ru(NCS)$_2$(IMesH$_2$)(C$_5$H$_5$N)(CHC$_6$H$_5$)] (1f). **1a** was dissolved in benzene (10 mL), and a solution of AgSCN (57.5 mg, 0.346 mmol) in benzene (2 mL) was slowly added to the solution, which was stirred at room temperature for 2 h. Complete chloride exchange was accompanied by a color change to dark green. The solvent was evaporated to dryness, the residue was dissolved in CH_2Cl_2 and filtered through Celite, and then the filtrate was concentrated to dryness. The residue was washed with pentane (3 × 15 mL) and dried. Recrystallization from CH_2Cl_2 /pentane at −50 °C afforded a green solid in 89% yield (102 mg, 0.147 mmol). ^{1}H NMR (CD_2Cl_2): δ = 17.79 (s, 1H, RuC*H*), 8.40 (bs, 2H, py, *o*-C*H*), 7.72 (bs, 1H, py, *p*-C*H*), 7.48 (bs, 2H, Ph, *o*-C*H*), 7.42 (t, J_{H-H} = 7.2 Hz, 1H, Ph, *p*-C*H*), 7.12 (t, 2H, J_{H-H} = 7.2 Hz, py, *m*-C*H*), 7.03 (bs, 2H, Ph, *m*-C*H*), 6.65 (bs, 4H, Ar, Mes-C*H*), 3.94 (s, 4H, CH_2CH_2), 2.38 (s, 12H, Mes-CH_3), 2.11 (s, 6H, Mes-CH_3). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ = 322.1 (m, Ru=CHPh), 212.8 (NCN), 151.8, 150.3, 138.0, 137.3, 136.5, 135.7, 130.9, 129.9, 128.6, 124.6, 124.3, 123.8, 52.4, 52.2, 22.8, 21.2. FT-IR (ATR mode): 3520 (w), 2914 (w), 2097 (vs), 1601 (m), 1634 (m), 1485 (s), 1445 (s), 1416 (s), 1262 (vs), 1216 (m), 1174 (m), 1068 (m), 1039 (m), 873 (m), 851 (m), 808 (m), 755 (m), and 698 cm^{-1} (m). HRMS (ESI) calcd for $C_{35}H_{37}N_5S_2Ru^+$: 693.153 39; found: 693.162 30 $[M]^+$.

[Ru(NO$_3$)$_2$(IMesH$_2$)(CH-2-(2-PrO)-C$_6$H$_4$)] (2d). $RuCl_2$(IMesH$_2$)(CH-2-(2-PrO)-C_6H_4)] (200 mg, 0.32 mmol) was dissolved in 5 mL of CH_2Cl_2. A solution of $AgNO_3$ (113.8 mg, 0.67 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring at room temperature was continued for another hour, and a color change from green to dark brown was observed. The solvent was removed *in vacuo*, and the remaining material was redissolved in CH_2Cl_2 and filtered through Celite. Then, the filtrate was dried. The resulting material was washed with pentane (3 × 15 mL) and recrystallized from CH_2Cl_2/pentane at −50 °C, affording a brown solid in 84% yield (182 mg, 0.268 mmol). ^{1}H NMR ($CDCl_3$): δ = 18.63 (s, 1H, Ru=C*HAr*,), 7.55 (t, J_{H-H} = 7.2 Hz, 1H), 7.34 (d, J_{H-H} = 7.2 Hz, 1H), 7.06 (t, J_{H-H} = 7.2, 1H), 6.96 (s, 4H), 6.89 (d, J_{H-H} = 8.4 Hz 1H), 4.83 (q, J_{H-H} = 6.6 Hz, 1H, CH), 4.05 (s, 4H, CH_2CH_2), 2.42 (s, 12H, CH_3), 2.42 (s, 12H, CH_3), 2.28 (s, 6H, CH_3), 1.2

(d, J_{H-H} = 6.6 Hz, 6H, CH_3). ^{13}C {^1H} NMR ($CDCl_3$): δ = 321.4 (m, Ru=CHPh), 198.5 (NCN), 155.26, 144.41, 138.5, 136.9, 135.9, 131.9, 129.3, 123.9, 123.1, 113.7, 77.0, 52.5, 21.2, 20.0, 18.15. FT-IR (ATR mode): 2918 (w), 2097 (w), 1588 (m), 1495 (vs), 1454 (m), 1417 (m), 1295 (s), 1256 (vs), 1210 (w), 1160 (w), 1097 (m), 1037 (m), 1007 (m), 927 (m), 850 (m), 786 (m), 751 (m), and 698 cm^{-1} (m). Elemental analysis calcd for $C_{31}H_{38}N_4O_7Ru$: (679.73 g/mol): C 54.78, H 5.63, N 8.24; found: C 54.33, H 5.73, N 8.05.

[Ru(CF$_2$)$_3$(COO)$_2$(IMesH$_2$)(CH-2-(2-PrO)-C$_6$H$_4$)] (2f). $RuCl_2$-$(IMesH_2)$(=CH-2-(2-PrO)-C_6H_4)] (200 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (5 mL). A suspension of [$(CF_2)_3(CO_2Ag)_2$] (113.8 mg, 0.67 mmol) in CH_2Cl_2 (2 mL) was slowly added. The mixture was stirred at room temperature for 1 h; complete chloride exchange was accompanied by a color change from green to red-brown. The mixture was filtered through Celite and the filtrate was evaporated to dryness. The residue was washed with pentane (3 × 15 mL) and dried. Recrystallization from CH_2Cl_2/pentane at −50 °C afforded a red-brown solid in 86% yield (212 mg, 0.267 mmol). ^1H NMR ($CDCl_3$): δ 17.34 (t, J_{H-H} = 13.8 Hz, 1H RuC*H*,), 7.22 (bs, 1H), 7.06 (m, 5H), 6.85 (t, J_{H-H} = 7.2 Hz, 1H), 6.46 (d, J_{H-H} = 7.8 Hz 1H), 4.41 (q, J_{H-H} = 5.4 Hz, 1H, CH), 4.03 (s, 4H, CH_2CH_2), 2.39 (s, 6H, CH_3), 2.18 (bs, 12H, CH_3), 0.84 (m, 6H, CH_3). ^{13}C {^1H} NMR ($CDCl_3$): δ = 315.6 (t, Ru=CHPh), 210.5, 161.2, 153.2, 143.3, 140.8, 139.7, 139.1, 136.9, 129.7, 128.8, 128.48, 126.7, 124.2, 122.6, 111.0, 108.6, 106.7, 74.4, 53.6, 52.6, 21.3, 20.0, 18.0. ^{19}F NMR (CD_2Cl_2, 564.8 MHz): δ = −112.4, −112.9, −116.3, −116.8, −121.0, −121.7. FT-IR (ATR mode): 2918 (w), 1692 (vs), 1607 (m), 1579 (m), 1479 (m), 1454 (m), 1333 (m), 1261 (s), 1153 (vs), 1113 (m), 1045 (m), 939 (m), 913 (m), 989 (m), 843 (m), 796 (m), and 745 cm^{-1} (m). HRMS (ESI) calcd for $C_{36}H_{38}F_6N_2O_5Ru^+$: 794.172 84; found: 744.186 52 $[M-CF_2]^+$.

Typical Copolymerization Procedure. Initiator **5a** (2.0 mg, 0.0032 mmol) dissolved in 0.5 mL of CH_2Cl_2 was added to a solution of NBE (300 mg, 3.18 mmol) and CPE (218 mg, 3.18 mmol) in 2 mL of CH_2Cl_2. The reaction mixture was stirred for 2 min. Then the reaction was stopped by the addition of ethyl vinyl ether, and the polymer was precipitated by the dropwise addition of the reaction mixture into methanol. The precipitated polymer was collected by filtration and washed with an excess methanol and dried *in vacuo*.

Typical Homopolymerization Procedure. Initiator **2b** (2 mg, 0.0031 mmol) dissolved in 0.5 mL of CH_2Cl_2 was added to a solution of cyclopentene (210 mg, 3.08 mmol) in 1 mL of CH_2Cl_2. The reaction mixture was allowed to stir for 5 h at 50 °C. After 5 h, the reaction was stopped by the addition of ethyl vinyl ether, and the polymer was precipitated by the dropwise addition of the solution into methanol. The precipitated polymer was collected by filtration and washed with an excess methanol and dried *in vacuo*.

■ ASSOCIATED CONTENT

Supporting Information. Results for the homopolymerization of NBE and COE, copolymerization parameters, selected ^1H and ^{13}C NMR spectra of homopolymers and alternating copolymers, selected kinetic plots for homo- and copolymerizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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