Articles

Bi- and Trinuclear Ruthenium Alkylidene Triggered Cyclopolymerization of 1,6-Heptadiynes: Access to A_n-X-A_n Block and $(A_n)_3X$ Tristar Copolymers

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ABSTRACT: Benzoic acid (4-(2-propoxy)-3-vinylphenyl) ester (**1**), the divinyl compounds terephthalic acid bis(4-(2-propoxy)-3-vinylphenyl) ester (**2**) and bis(4-(2-propoxy)-3-vinylphenoxy)diphenylsilane (**3**), and the trivinyl compound benzene-1,3,5-tricarboxylic acid tris(4-(2-propoxy)-3-vinylphenyl) ester (**4**) were used for the synthesis of a series of ruthenium-based mono-, bi-, and trinuclear metathesis catalysts, i.e., $RuX_2(IMesH_2)$(=CH-2-(2-PrO)-C_6H_3-5-$OOCC_6H_5$) (X = Cl, **I1a**; X = $OOCCF_3$, **I1b**), 1,4-[$RuX_2(IMesH_2)$(=CH-2-(2-PrO)-C_6H_3-5-OOC)]$_2C_6H_4$ (X = Cl, **I2a**; X = $OOCCF_3$, **I2b**), [$RuX_2(IMesH_2)$(=CH-2-(2-PrO)-C_6H_3-5-O)]$_2SiPh_2$ (X = Cl, **I3a**; X = $OOCCF_3$, **I3b**), and 1,3,5-[$RuX_2(IMesH_2)$(=CH-2-(2-PrO)-C_6H_3-5-OOC)]$_3C_6H_3$ (X = Cl, **I4a**; X = $OOCCF_3$, **I4b**) ($IMesH_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene), where the corresponding trifluoroacetate-derived systems were prepared from the parent dichloro-substituted initiators via reaction with CF_3COOAg. Initiators **I1a**−**I4a** and **I1b**−**I4b** were used for the cyclopolymerization of a series of 1,6-heptadiynes, i.e., dimethyl dipropargylmalonate (**M1**), diethyl dipropargylmalonate (**M2**), di-*tert*-butyl dipropargylmalonate (**M3**), 4-(ethoxycarbonyl)-1,6-heptadiyne (**M4**), 4,4-(bishydroxymethyl)-1,6-heptadiyne (**M5**), and 4-(hydroxymethyl)-1,6-heptadiyne (**M6**), to yield the corresponding A_n-X-A_n type block and $(A_n)_3X$ type tristar copolymers. Cleavage of the A_n-X-A_n type block copolymer **M2**$_{25}$−CH-[2-(2-PrO)-1,5-C_6H_3]-O-$SiPh_2$-O-[2-(2-PrO)-1,5-C_6H_3]-CH-**M2**$_{25}$ with tetrabutylammonium fluoride resulted in the formation of the low-PDI telechelic homopolymer **M2**$_{25}$-CH-[2-(2-PrO)-1,5-C_6H_3]-OH with half the molecular weight of the parent block copolymer, indicative for an equal activity of both initiator sites in **I3b**. An interesting finding was the fact that monomers with reduced steric demands in the 4-position (**M1**, **M4**, **M5**, and **M6**) could even be polymerized with chlorine-based initiators; however, values for M_n were in general lower than the calculated ones. In contrast to Mo-based initiators, no influence of monomer size on the structure of the final polymer in terms of the ratio of 1,2-(cyclopent-1-ene)-vinylene and 1,3-(cyclohex-1-ene)methylidene units, respectively, was observed.

Introduction

In the course of our investigations on the living cyclopolymerization of 1,6-heptadiynes, we have elaborated on a series of molybdenum-based Schrock-type[1−6] and ruthenium-based Grubbs-type initiators[7−11] that are capable of fulfilling this task in a stereo- and regioselective manner. Together with the molybdenum-based initiators developed in the Schrock group in the mid-1990s,[12,13] one disposes now over an armor of initiators that allows the selective formation of conjugated polyene-type polymers based on either a 1,2-(cyclopent-1-ene)-vinylene or 1,3-(cyclohex-1-ene)methylidene backbone.[14] Recently, using ruthenium-type initiators, we were able to extend this concept to the cyclopolymerization of 1,6-heptadiynes bearing protic, i.e., hydroxyl and carboxylic acid groups.[15,16] We now turned our interest to the synthesis of bi- and trinuclear initiators. In this context, the attractiveness of such initiators is obvious. Thus, binuclear initiators offer straightforward access to A−B−A triblock (i.e., pseudo-A−B−X−B−A pentablock) copolymers by one single change in monomer type during polymerization. This method becomes particularly attractive in case the synthesis of A−B−A block copolymers via reaction of (living) A with B to form a living A−B block copolymer is possible; however, subsequent reaction of this living diblock copolymer with A to form the desired A−B−A triblock copolymer is impossible.[17] The fact that synthesis is accomplished in one single step puts also reduced demands on the livingness of the entire system, thus broadening the range of catalysts that may be used for these purposes. In addition, no AB diblock copolymers are formed as byproducts. Finally, such initiators also offer access to symmetrical ditelechelic polymers. Similarly, trifunctional initiators offer access to star-type polymers. Such polymers have been extensively studied

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due to their branched structures and unique physicochemical properties different from those of their linear polymeric counterparts. Because of their spherical shape, star polymers have properties and even functions different from their linear counterparts.[18−20] In this context, particularly their rheological properties and aggregation behavior are in the center of interest. Numerous authors already reported on the synthesis of a series of multifunctional initiators[21] and their use in ring-opening metathesis polymerization (ROMP) and cyclopolymerization.[22−27] Masuda et al. reported on the synthesis of star-type polymers based on the living 1-alkyne polymerization of phenylacetylene and 2-(trifluoromethyl)phenylacetylene mediated by Rh- and Mo-based catalysts, respectively.[28,29] Here, we wish to report our latest results on the synthesis of novel bi- and trinuclear ruthenium-based initiators and their use in the cyclopolymerization of various 1,6-heptadiynes. The new initiators give rise to novel, unprecedented, cyclopolymerization-derived polymer architectures such as block as well as tristar copolymers.

Results and Discussion

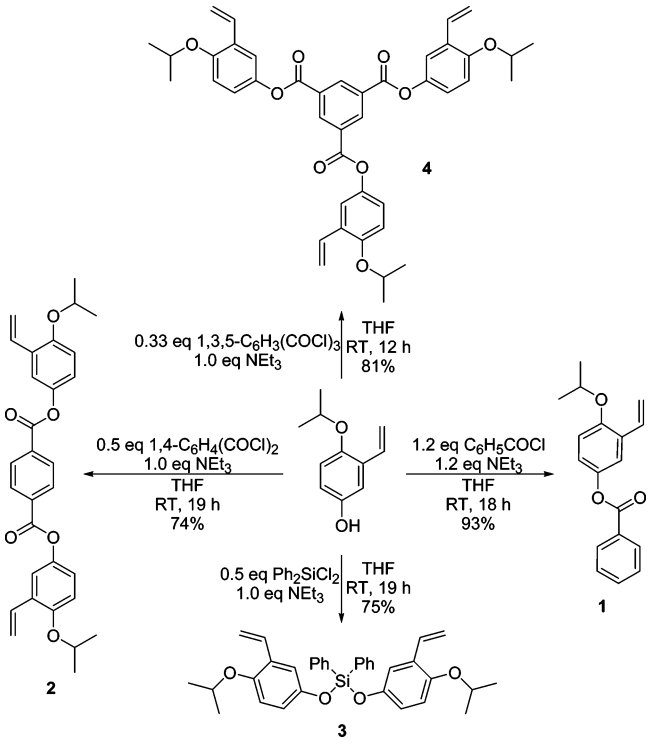
Ligand Synthesis. Four different 2-(2-propoxy)styrene-based ligands **1**−**4** were prepared for the present investigation (Scheme 1). All ligand systems were accessible following a modular approach starting from 5-hydroxy-2-(2-propoxy)styrene as a universal precursor. 5-Hydroxy-2-(2-propoxy)styrene was synthesized in a four-step reaction sequence from 2,5-dihydroxybenzaldehyde as described by Yao.[30] Coupling of 5-hydroxy-2-(2-propoxy)styrene to the corresponding aryl acid chlorides benzoyl chloride, terephthaloyl chloride, and trimesoyl trichloride provided **1**, **2**, and **4**, respectively. The introduction of a fluoride-labile silyl linker resulted in ligand system **3**, which was accomplished via silylation of the hydroxyl group of 5-hydroxy-2-(2-propoxy)styrene using dichlorodiphenylsilane (Scheme 1).

It is worth mentioning that the sterically more demanding dichlorodiphenylsilane turned out to be superior over dichlorodimethylsilane since it significantly reduced hydrolysis, which was observed to a notable extent during the purification of crude dimethylsilyl-bridged species in the course of column chromatography.

Synthesis of Ruthenium Complexes I1a−**I4b.** Initiators **I1a**−**I4a** were prepared according to a procedure published by Hoveyda and co-workers.[21] Treatment of $RuCl_2(IMesH_2)(PCy_3)$-(=CHPh) (second-generation Grubbs catalyst) with the appropriate amounts of ligands **1**−**4** in the presence of CuCl in CH_2Cl_2 at 40 °C followed by column chromatography afforded the desired 2-(2-propoxy)styrene-derived complexes **I1a**−**I4a** as bright green solids in 42−73% isolated yields (Scheme 2). In the case of **I3a**, the Si−O bond proved to be susceptible to partial hydrolysis upon purification, thus explaining the comparably low yield of **I3a** (42%). As depicted in Scheme 2, both chlorines per ruthenium center could be substituted in **I1a**−**I4a** by electron-withdrawing trifluoroacetates. Reaction of **I1a**−**I4a** with 2 equiv of silver trifluoroacetate per ruthenium center in THF offered access to complexes **I1b**−**I4b** in virtually quantitative yields. Unfortunately, in contrast to mononuclear compounds,[7,10,31] removal of traces of AgCl by chromatography on silica or alumina turned out to be accompanied by significantly reduced yields for compounds **I1b**−**I4b**.

Cyclopolymerizations. The principles of cyclopolymerization including the two different reaction pathways that offer access to polyenes containing either five-membered (i.e., 1,2-(cyclopent-1-ene)vinylene) or six-membered (i.e., 1,3-(cyclohex-1-ene)methylidene) ring-based repetitive units are well-understood

Scheme 1. Synthetic Route to 2-(2-Propoxy)styrene-Derived Ligands 1−4



(Scheme 3)[24,32] and have been summarized elsewhere.[14,33,34] On the basis of an "alkylidene mechanism" proposed for the cyclopolymerization of 1,6-heptadiyne derivatives,[32] the backbone structure of the polymer exclusively depends on the mode of addition, i.e., α- or *β*-addition, of the monomer to the M=C bond in the initial step.

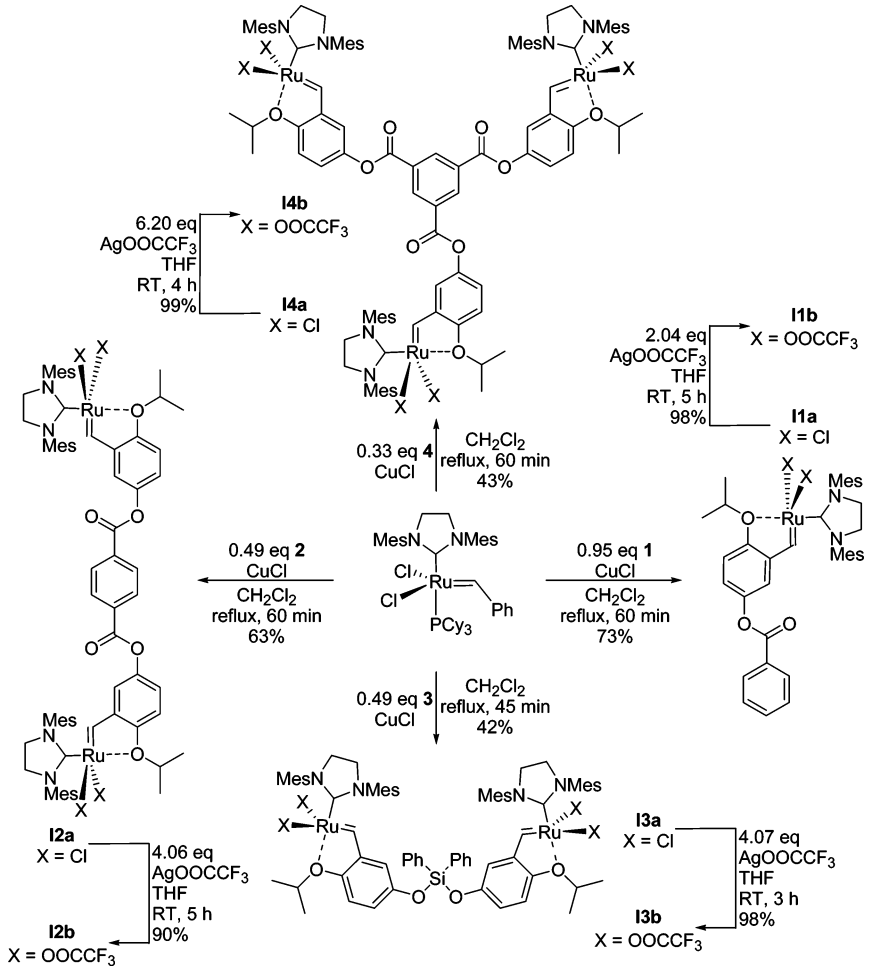
This initial step is responsible for the ring size of the repeating units. In the case of Mo-based Schrock-type initiators, both the *steric* and *electronic* effects of the ligand sphere around the M=C bond of the initiator[4,5,9,13] as well as the steric demands of the substituents in the 4-position of the 1,6-heptadiyne[4,5,27,35] exert decisive influence on the regio- and stereoselectivity of the cyclopolymerization.

To get some further insight into both the steric effects and the influence of the polarity of the substituents in the 4-position on the cyclopolymerization mediated by the ruthenium-based initiators **I1a**−**I4b**, we chose six 1,6-heptadiyne derivatives **M1**−**M6** as model monomers (Figure 1). So far, the cyclopolymerization of both **M2** and **M4** by the action of Ru-$(CF_3COO)_2(IMesH_2)$-derived initiators yielded polyenes exclusively based on 1,2-(cyclopent-1-ene)vinylene units.[7−9,15,16] We were therefore interested in whether polymer structure was generally based on 1,2-(cyclopent-1-ene)vinylenes with this type of catalysts or, similar to Mo-based initiators,[1,4−6,12,13,24,32] dependent on monomer size, thus offering access to polyenes selectively based on either 1,2-(cyclopent-1-ene)vinylene or 1,3-(cyclohex-1-ene)methylidenes or at least mixtures thereof.

The monomers dimethyl dipropargylmalonate (**M1**),[36] diethyl dipropargylmalonate (**M2**),[37] di-*tert*-butyl dipropargylmalonate (**M3**),[27] 4-(ethoxycarbonyl)-1,6-heptadiyne (**M4**),[24] 4,4-(bishydroxymethyl)-1,6-heptadiyne (**M5**),[24] and 4-(hydroxymethyl)-1,6-heptadiyne (**M6**)[15] were prepared according to published procedures.

Polymerization of M1−**M6 Induced by Mono-, Bi-, and Trinuclear Ruthenium-Based Initiators.** Our interest first focused on the potential of **I1a** and **I1b** as initiators for the

Scheme 2. Synthesis of Grubbs−Hoveyda-Type Alkylidenes I1a−I4a and I1b−I4b

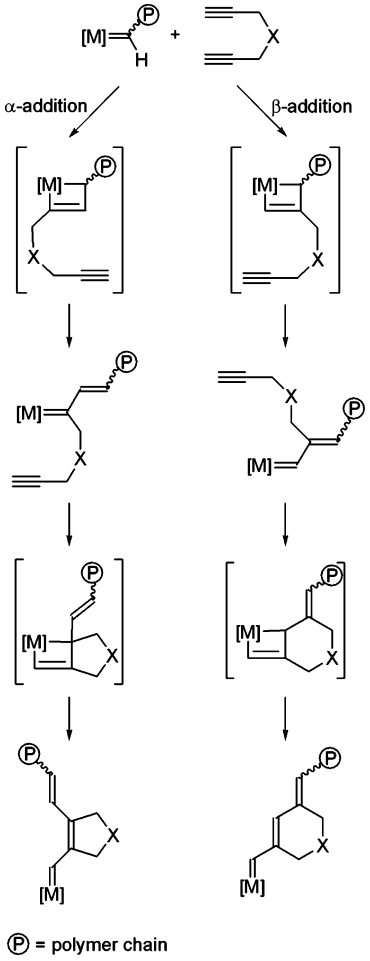


cyclopolymerization of **M2** and **M4**, bearing medium-sized and comparably small substituents in the 4-position. Initiators **I1a** and **I1b** may be regarded mononuclear mimics of the bi- and trinuclear complexes **I2a**−**I4b**. In accordance with earlier findings,[9] chlorine-based **I1a** was almost inactive in the polymerization of **M2**, though the initially greenish initiator solution turned red after **M2** was added, indicative of monomer addition to the Ru=C bond. However, only traces of methanol insoluble oligomers were formed as GPC measurements revealed (Table 1). Therefore, exchange of the chloro ligands in **I1a** by the more electron-withdrawing trifluoroacetates was carried out to result in **I1b**. This initiator turned out to be active for the polymerization of **M2** (Table 2).

In contrast to these findings, polymerization of **M4**, with reduced steric demands in the 4-position, yielded deeply colored poly-**M4** using either **I1a** or **I1b**, as has been reported for similar initiators.[15] However, the more reactive trifluoroacetate-based **I1b** resulted in ca. 30% higher yields of isolated poly-**M4**, and the degree of polymerization could only be influenced by the initial monomer-to-initiator ratio by using **I1b** as initiator (Table 2). In contrast, chlorine-based **I1a** led to poly-**M4** in moderate yields (21−36%) with molecular weights of roughly 6000 g/mol, irrespective of the monomer-to-initiator ratio adjusted (Table 1). So far, the only profound explanation for the substrate specific reactivity of chlorine-based initiators of type **I1a** we can come up with is that, besides reduced steric demands, the alkyne groups in **M4** are (slightly) more electron rich compared to those in **M2**, a fact that has proven important for other types of monomers in 1-alkyne polymerization.[38]

Since initiators of type **I1a** or **I1b** with aryl ester substituents in the 5-position were active in the cyclopolymerization of 1,6-heptadiyne derivatives, we decided to further investigate their bi- and trinuclear analogues **I2a**, **I2b**, **I4a**, and **I4b**. Poly-**M1** synthesized with initiators **I2a**, **I2b**, **I4a**, and **I4b** showed low solubility in common solvents, such as CH_2Cl_2 or $CHCl_3$. This is believed to be a monomer (polymer)-specific property. Thus, **M1** polymerized by the action of **I2b** in the presence of 3-Br-pyridine[39] gave identical results in terms of solubility. Especially the initiators **I2b** and **I4b** bearing trifluoroacetato ligands furnished poly-**M1** with dramatically reduced solubility. Therefore, detailed polymer characterization was virtually impossible. Whereas the chlorine-based initiators **I2a** and **I4a** induced the cyclopolymerization of **M1**, only oligomers were obtained from **M2** and **M3**, which contain sterically more demanding substituents in the 4-position (Table 1). However, changing from the chlorine-based initiators **I2a** and **I4a** to the trifluoroacetate-based ones gave rise to moderate yields for **M3** (ca. 20%, Table 2) and high yields for **M2** (up to 95%, Supporting Information). As observed for the mononuclear mimic **I1a**, **M4** bearing a rather small substituent in the 4-position could be polymerized with chlorine-derived initiators **I2a** and **I4a** (Table 1). However, isolated yields of the polymer were again significantly higher when the more active initiators **I2b**, **I3b**, and **I4b** were used instead (Table 2). Finally, both the chlorine-based initiators **I2a** and **I4a** as well as the trifluoroacetate-derived complexes **I2b** and **I4b** were capable of polymerizing the sterically less demanding and highly polar monomers **M5** and **M6** to afford polyenes which were only partially soluble in polar solvents

Scheme 3. Two Possible Reaction Pathways for the Cyclopolymerization of 1,6-Heptadiynes



like dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylacetamide (DMAc).

Livingness of Cyclopolymerizations. Correlation plots of M_n vs the number of monomer equivalents (N) revealed a linear dependence for polymerizations of **M2** and **M4** mediated by the binuclear system **I2b**, indicating a controlled cyclopolymerization (Figure 2).

Using a monomer-to-initiator ratio of 10, reinitiation with additional 100 equiv of monomer occurred only partially (~80%) for the system **M2-I2b** after 8.5 h. This suggests at least a class IV living system for **M2-I2b** according to the ranking of Matyjaszewski.[40] Disappointingly, even after only 3.5 h virtually no reinitiation was observed for the system **M4-I2b** indicative for a class III or IV living system. A class I and II living system may be excluded in view of the time needed to synthesize poly-**M4** with a degree of polymerization of 90 (typically more than 5 min). In the case of poly-**M2** prepared by the action of **I2b**, PDIs were in the range of 1.6−1.9, which is also indicative for a nonperfect living behavior. In this context, values for the ratio of the rate constants for propagation and initiation, k_p/k_i, need to be considered. This ratio can be determined by ^{1}H NMR[41] and is an important aspect in terms of the initiation efficiency of a polymerization system. For the system **M2-I2b**, a value of $k_p/k_i > 1000$ was estimated[5] and accounts at least in part for the positive deviation in the correlation plot. Additional deviations stem from measurements vs poly(styrene) (PS) standards.[4] The system **M4-I2b** afforded poly-**M4** with comparably low PDIs ($1.29 \leq$ PDI ≤ 1.39, Supporting Information); however, the value for k_p/k_i was >1000 as well. As reported recently for other Ru-based initiators,[15] the observed molar masses were lower than the calculated ones for degrees of polymerization >40 (Figure 2, Supporting Information).

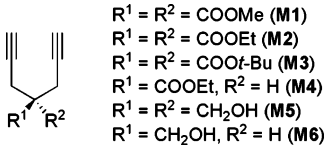


Figure 1. Structures of monomers **M1**−**M6**.

Having established the principal reactivity of this type of initiator, the ruthenium-based Grubbs-Hoveyda-type complexes **I2b**, **I3b**, and **I4b** were screened as initiators for the cyclopolymerization of **M1**−**M6** (Table 2 and Supporting Information). Polymerizations of **M1**−**M4** and **M6** by any ruthenium-based initiator were performed in CH_2Cl_2. Dark purple-black powders were obtained after terminating the reaction with excess ethyl vinyl ether, removal of the solvent, and extraction of the residue with methanol. Cyclopolymerization of **M5** mediated by any ruthenium-based initiator was conducted in a solvent mixture of CH_2Cl_2 and methanol due to the lack of solubility of **M5** in CH_2Cl_2.[15] Molecular weights of the polymers were determined by GPC vs PS in $CHCl_3$ for poly-**M1**, poly-**M2**, poly-**M3**, and poly-**M4** or vs poly(methyl methacrylate) (PMMA) in DMAc for highly polar poly-**M5** and poly-**M6**.

Taking the high values for the ratio of k_p/k_i of the monomer-ruthenium-based initiator systems investigated in our studies into account, we were curious to get some evidence if really all

Table 1. GPC, UV−Vis Data, and Yields for Polyenes Prepared Using the Chlorine-Based Initiators I1a, I2a, and I4a[a]

initiator	polymer	M_n(calcd) (g/mol)[b]	M_n (g/mol)[c]	M_w/M_n[c]	λ_{max} (nm)[d]	yield (%)[e]
I1a	poly-**M2**$_{50}$	12100	<1000	1.01[f]	529	<3
I1a	poly-**M4**$_{50}$	8500	6100	1.67	570[g]	36
I1a	poly-**M4**$_{100}$	16700	5800	1.79	570[g]	21
I2a	poly-**M1**$_{52}$	11300	4200	1.26	501	32
I2a	poly-**M2**$_{52}$	12800	<1000	1.01[f]	498	<3
I2a	poly-**M3**$_{47}$	14200	<1000	1.04[f]	570[g]	<3
I2a	poly-**M4**$_{83}$	14100	6800	1.59	570[g]	28
I2a	poly-**M5**$_{47}$	7600	16600[h,i]	2.11[h,i,j]		74
I2a	poly-**M6**$_{70}$	9000	5200[h,i]	1.30[h,i]		71
I4a	poly-**M1**$_{59}$	13000	4200	1.36	495	21
I4a	poly-**M2**$_{78}$	19100	<1000	1.01[f]	498	<3
I4a	poly-**M4**$_{103}$	17600	9400	1.70[j]	570[g]	46
I4a	poly-**M5**$_{103}$	16400	12200[h,i]	2.04[h,i,j]		69
I4a	poly-**M6**$_{113}$	14500	4000[h,i]	1.41[h,i]		68

[a] Details of the procedure are described in the Experimental Section. [b] Assuming 100% conversion, including end groups. [c] Determined by GPC vs PS with the RI detector in $CHCl_3$. [d] In $CHCl_3$ at room temperature. [e] Determined by gravimetry. [f] Minor higher molecular weight fractions in GPC. [g] Shoulder. [h] Determined by GPC vs PMMA with the RI detector in DMAc. [i] DMAc-soluble fraction. [j] High molecular weight shoulder/tailing.

Table 2. GPC, UV−Vis Data, and Yields for Polyenes Prepared Using the Trifluoroacetate-Based Initiators I1b, I2b, I3b, and I4b[a]

initiator	polymer	M_n(calcd) (g/mol)[b]	M_n (g/mol)[c]	M_w/M_n[c]	λ_{max} (nm)[d]	yield (%)[e]
I1b	poly-**M2**$_{50}$	12100	22500	2.04	586	63
I1b	poly-**M4**$_{50}$	8500	6700	1.63	570[f]	65
I1b	poly-**M4**$_{100}$	16700	8700	1.55	570[f]	50
I2b	poly-**M1**$_{70}$	15100	5900[g]	1.60[g]	507	17
I2b	poly-**M2**$_{50}$	12300	19000	1.78	586	76
I2b	poly-**M3**$_{50}$	15100	9600	1.30	576	∼20
I2b	poly-**M4**$_{50}$	8700	7200	1.35	570[f]	59
I2b	poly-**M5**$_{50}$	8100	15600[h,i]	1.98[h,i,j]		64
I2b	poly-**M6**$_{50}$	6600	4400[h,i]	1.35[h,i]		25
I3b	poly-**M2**$_{50}$	12300	23300	1.66	584	62
I4b	poly-**M1**$_{70}$	15300	7300[g]	1.38[g]	530	52
I4b	poly-**M2**$_{50}$	12500	18900	1.71	580	86
I4b	poly-**M4**$_{70}$	12200	10600	1.51	570[f]	75
I4b	poly-**M5**$_{50}$	8300	14700[h,i]	1.83[h,i,j]		48
I4b	poly-**M6**$_{70}$	9200	5200[h,i]	2.43[h,i]		21

[a] Details of the procedure are described in the Experimental Section. [b] Assuming 100% conversion, including end groups. [c] Determined by GPC vs PS with the RI detector in $CHCl_3$. [d] In $CHCl_3$ at room temperature. [e] Determined by gravimetry. [f] Shoulder. [g] $CHCl_3$-soluble fraction. [h] Determined by GPC vs PMMA with the RI detector in DMAc. [i] DMAc-soluble fraction. [j] High molecular weight shoulder/tailing.

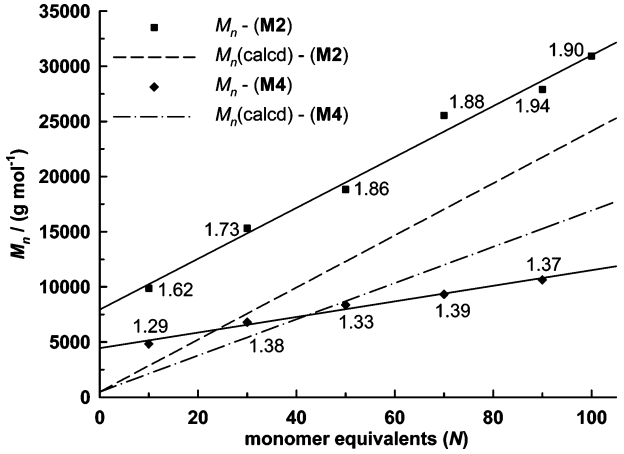


Figure 2. Plot of M_n vs number of monomer equivalents (N) and PDIs for a series of samples of **M2**$_n$-CH-[2-(2-PrO)-1,5-C_6H_3]-O-CO-1,4-C_6H_4-COO-[2-(2-PrO)-1,5-C_6H_3]-CH-**M2**$_n$ and **M4**$_n$-CH-[2-(2-PrO)-1,5-C_6H_3]-O-CO-1,4-C_6H_4-COO-[2-(2-PrO)-1,5-C_6H_3]-CH-**M4**$_n$ prepared by the action of **I2b** (data from Supporting Information).

ruthenium centers present in the initiators take part in the polymerization process or if polymerization proceeds predominantly through one active center. To address this question, we prepared a block copolymer, **M2**$_{25}$-CH-[2-(2-PrO)-1,5-C_6H_3]-O-$SiPh_2$-O-[2-(2-PrO)-1,5-C_6H_3]-CH-**M2**$_{25}$, using **I3b** as initiator. In **I3b**, the two ruthenium centers are connected via a siloxane linker susceptible to fluorine cleavage. A value for $k_p/k_i > 1000$ was again estimated for this polymerization system. In due consequence, the observed M_n of 23 300, PDI = 1.66, was higher than the calculated one (M_n(calcd) = 12 300 g/mol). However, treatment of **M2**$_{25}$-CH-[2-(2-PrO)-1,5-C_6H_3]-O-$SiPh_2$-O-[2-(2-PrO)-1,5-C_6H_3]-CH-**M2**$_{25}$ with excess *N*-tetrabutylammonium fluoride in CH_2Cl_2 resulted in the quantitative cleavage of the precursor polymer and the formation of a homopolymer with an M_n of 11 800 (Figure 3). The PDI remained virtually unchanged (PDI = 1.52). We therefore propose that both ruthenium centers exhibit the same activity at least in the polymerization of **M2**.

Controlled Cyclopolymerization of M2 and M4 Induced by the Trinuclear Ruthenium-Based Initiator I4b. Finally, we directed our interest to the trinuclear initiator **I4b** opening access to tristar copolymers containing conjugated arms. As for the binuclear analogue **I2b**, we investigated the polymerizations of **M2** and **M4** in some more detail. Similar to the binuclear system, correlation plots of M_n vs the number of monomer

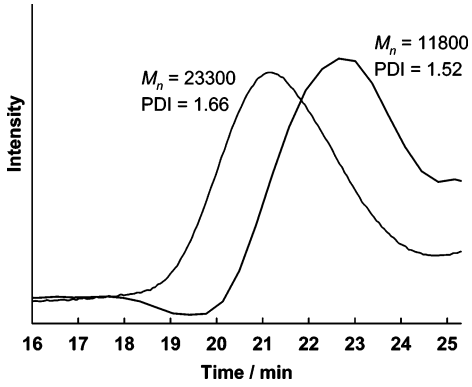


Figure 3. GPC (in $CHCl_3$) vs PS with RI detection of the cleavage of **M2**$_{25}$-CH-[2-(2-PrO)-1,5-C_6H_3]-O-$SiPh_2$-O-[2-(2-PrO)-1,5-C_6H_3]-CH-**M2**$_{25}$ prepared using **I3b**.

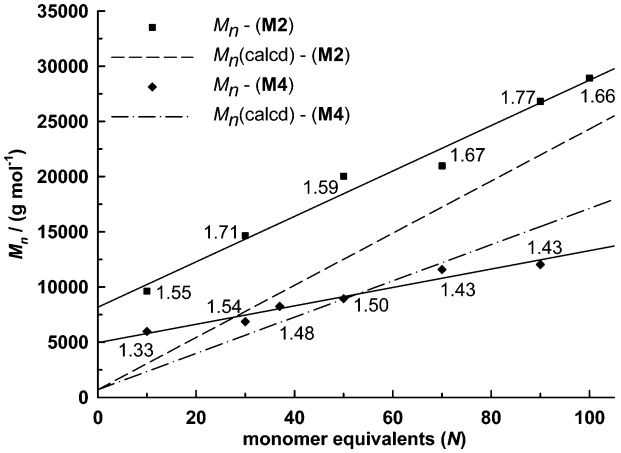


Figure 4. Plot of M_n vs number of monomer equivalents (N) and PDIs for a series of samples of {**M2**$_n$-CH-[2-(2-PrO)-1,5-C_6H_3-O-CO)]}$_3$-1,3,5-C_6H_3 and {**M4**$_n$-CH-[2-(2-PrO)-1,5-C_6H_3-O-CO]}$_3$-1,3,5-C_6H_3 prepared using **I4b** (data from Supporting Information).

equivalents (N) showed a linear relationship for both poly-**M2** and poly-**M4** (Figure 4).

Together with the comparably low PDIs (1.33 ≤ PDI ≤ 1.77; Figure 4, Supporting Information), these observations revealed fairly good control in the cyclopolymerization of **M2** and **M4**, though k_p/k_i values were again unsatisfactorily high with these systems ($k_p/k_i > 1000$).

Microstructure of Polymers. As can be deduced from the representative UV−vis spectra of **I2b**-derived poly-**M2**, poly-**M3**, and poly-**M4** depicted in Figure 5, two well-resolved

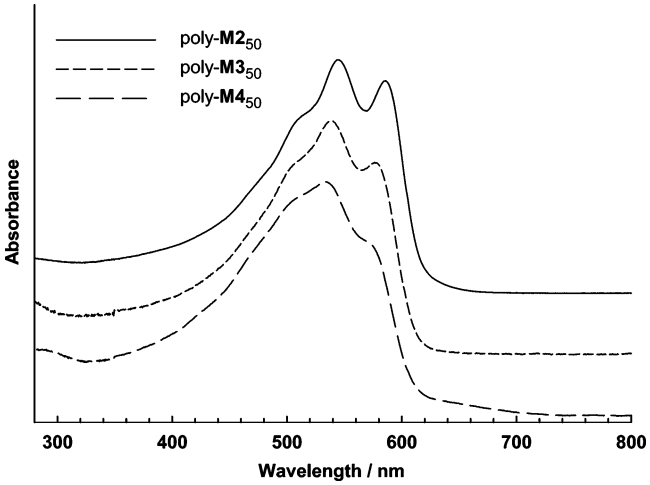


Figure 5. UV−vis spectra of poly-**M2**$_{50}$, poly-**M3**$_{50}$, and poly-**M4**$_{50}$ prepared using initiator **I2b** (polymers from Table 2, measured in $CHCl_3$ at room temperature).

absorption maxima at ca. 545 and 570−586 nm indicated regular polyenes with defined and uniform backbone structures.[42] According to the literature,[2,5,7,9] only poly(1,6-heptadiyne)s with pure five-membered-ring-based repeating units lead to absorption maxima (λ_{max}) in the range 580−590 nm.

To quantify the high content of 1,2-(cyclopent-1-ene)vinylene units expected from the UV−vis data, ^{13}C NMR spectra of poly-**M2**, poly-**M3**, and poly-**M4** were recorded.[4,5,24] On the basis of the chemical shifts of the carbonyl ($\delta(CO) = 171.5$ ppm) and quaternary carbon ($\delta(C(COOEt)_2) = 56.8$ ppm) and the number of signals that were observed in the ^{13}C NMR, a pure 1,2-(cyclopent-1-ene)vinylene structure could be assigned for all **M2**-derived polymers. The same accounts for poly-**M4** prepared by the action of initiators **I2b** and **I4b** ($\delta(CO) = 175.2$ ppm; $\delta(CHCOOEt)) = 39.7$ ppm). Similarly, the **I2b**-mediated cyclopolymerization of **M3** furnished poly-**M3** which consisted virtually exclusively (>99%) of 1,2-(cyclopent-1-ene)vinylene repeating units ($\delta(CO) = 170.7$ ppm; $\delta(C(COO\textit{t}\text{-}Bu)_2) = 57.7$ ppm), too; however, traces of residual monomer were observed in the ^1H NMR as well as the ^{13}C NMR spectra. Even after prolonged reaction times (up to 90 h) significant amounts of monomer could be detected. Whether this is indicative for termination reactions and/or attributable to the significant steric demands of **M3** remains speculative.

Conclusions

A series of novel bi- and trinuclear ruthenium-based initiators for the cyclopolymerization of 1,6-heptadiynes have been prepared. Using a bi- and trinuclear ruthenium alkylidene initiator, polymerization systems with good control over molecular weight have been realized for the polymerization of diethyl dipropargylmalonate (**M2**) and 4-(ethoxycarbonyl)-1,6-heptadiyne (**M4**), respectively. The polymerization of these two monomers with trifluoroacetate-based Grubbs−Hoveyda-type initiators yielded polymers with a well-defined microstructure of virtually 100% five-membered rings, i.e., 1,2-(cyclopent-1-ene)vinylene units. The fact that chain growth of a binuclear initiator proceeds in both directions to the same extent was proven by chain cleavage of a siloxane-bridged block copolymer, yielding a homopolymer with narrow polydispersity and half the molecular weight of the parent block copolymer. Other functional heptadiynes containing two methyl ester and one or two hydroxyl groups in the 4-position were also polymerized by both chlorine- and trifluoroacetate-derived mononuclear, dinuclear, and trinuclear ruthenium-based initiators. In contrast, 1,6-heptadiynes bearing two ethyl or *tert*-butyl ester pendants in the 4-position yielded the corresponding A_n-X-A_n type block and $(A_n)_3X$ type tristar copolymers only if trifluoroacetate-based initiators were employed. Finally, another important conclusion is that $Ru(CF_3COO)_2(IMesH_2)$-derived initiators *do not* allow for a monomer-dependent formation of cyclopolymerization-derived polymer structures. 1,2-(Cyclopent-1-ene)vinylene units are formed exclusively, which is in contrast to Mo-based initiators, which allow for the formation of both 1,2-(cyclopent-1-ene)vinylene and 1,3-(cyclohex-1-ene)methylidene units.

Experimental Section

General Details. Unless stated otherwise, all experiments were performed under an argon atmosphere in a MBraun drybox or by using standard Schlenk techniques. Reagent grade tetrahydrofuran and pentane were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane, chloroform-d_1, and triethylamine were distilled from calcium hydride under argon. Dichloromethane as polymerization solvent and chloroform-d_1 were passed over a plug of activated alumina prior to use. All other reagents were purchased from Aldrich or Fluka and used as received without further purification.

Dimethyl dipropargylmalonate (**M1**),[36] diethyl dipropargylmalonate (**M2**),[37] di-*tert*-butyl dipropargylmalonate (**M3**),[27] 4-(ethoxycarbonyl)-1,6-heptadiyne (**M4**),[24] 4,4-(bishydroxymethyl)-1,6-heptadiyne (**M5**),[24] 4-(hydroxymethyl)-1,6-heptadiyne (**M6**),[15] and 5-hydroxy-2-isopropoxystyrene[30] were prepared as described in the literature.

Column chromatography was performed on silica 60 (0.04−0.063 mm, Fluka, Buchs, Switzerland) or on neutral alumina (0.05−0.15 mm, Fluka, Buchs, Switzerland). Gel permeation chromatography (GPC) was carried out using PLgel 5 μm MIXED-C columns (PLgel 5 μm Guard, 50 × 7.5 mm, PLgel 5 μm MIXED-C, 300 × 7.5 mm, PLgel 5 μm MIXED-C, 600 × 7.5 mm), a 410 differential refractometer detector, and a 486 UV detector for measurements in $CHCl_3$ (all from Waters). The flow rate was set to 1.0 mL/min. Samples were filtered through a 0.2 μm Teflon filter (Macherey-Nagel) in order to remove particles. GPC columns were calibrated vs polystyrene (PS) standards (Polymer Standards Service (PSS), molecular weights 580−1.57 × 10^6 g/mol). Data were processed using a Millenium software. For measurements in *N*,*N*-dimethylacetamide (DMAc), GPC was carried out using PLgel 5 μm MIXED-C and PLgel 3 μm MIXED-E columns (PLgel 5 μm MIXED-C, 300 × 7.5 mm, PLgel 5 μm MIXED-C, 300 × 7.5 mm, PLgel 3 μm MIXED-E, 300 × 7.5 mm, PLgel 3 μm MIXED-E, 300 × 7.5 mm) and a 410 differential refractometer (RI) detector (Waters). The flow rate was set to 0.5 mL/min. Samples were filtered through a 0.2 μm Teflon filter (Macherey-Nagel) in order to remove particles. GPC columns were calibrated vs poly(methyl methacrylate) standards (Polymer Standards Service (PSS), molecular weights 960−1.64 × 10^6 g/mol). Data were processed using a Millenium software. UV−vis spectra were recorded on a Varian Cary 3 spectrophotometer in the range of 280−800 nm. Elemental analyses were performed at the Mikroanalytisches Labor, Department Chemie, Technische Universität München, Germany. NMR data were obtained at 300.13 MHz (^1H) and 75.47 MHz (^{13}C) on a Bruker ARX 300 and at 250.13 MHz (^1H) and 62.90 MHz (^{13}C) on a Bruker AC 250 spectrometer. Chemical shifts are listed in parts per million (ppm) downfield from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: ^1H: $\delta = 7.25$; ^{13}C: $\delta = 77.0$). FT-IR spectra were recorded on a Bruker Vector 22 or a Bruker IFS 55 spectrometer using ATR technology. ESI-MS spectra were acquired on a Finnigan LCQ spectrometer with acetonitrile/water as solvent.

Benzoic Acid (4-(2-Propoxy)-3-vinylphenyl) Ester (1). Benzoyl chloride (228.6 mg, 1.63 mmol) was added to a stirred solution of 5-hydroxy-2-(2-propoxy)styrene (241.5 mg, 1.35 mmol) in THF

(10 mL). After NEt_3 (164.5 mg, 1.63 mmol) was slowly added, the white suspension was stirred for 18 h at room temperature. The reaction mixture was diluted with water (40 mL) and extracted with diethyl ether (3 × 40 mL). The combined organic layers were washed with water (40 mL), and the solvent was removed under reduced pressure. The resultant material was dissolved in CH_2Cl_2, rotated onto silica, and purified by column chromatography (silica 60: hexane:ethyl acetate 10:1, $R_f = 0.4$). Evaporation of the solvent afforded **1** as a white solid (354.7 mg, 1.26 mmol, 93%). IR (ATR mode, cm^{-1}): 2983 (m); 2935 (w); 2873 (w); 1913 (w); 1822 (w); 1731 (s); 1652 (w); 1622 (w); 1600 (w); 1582 (w); 1482 (s); 1449 (m); 1424 (m); 1377 (m); 1337 (w); 1311 (w); 1247 (s); 1194 (m); 1175 (m); 1155 (m); 1139 (w); 1100 (m); 1057 (s); 1022 (m); 998 (m); 954 (m); 926 (w); 901 (m); 853 (w); 801 (w); 704 (s). ^{1}H NMR ($CDCl_3$): δ = 8.19 (m, 2H, Ph-H_o); 7.63 (tt, 1H, Ph-H_p, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz); 7.50 (m, 2H, Ph-H_m); 7.31 (d, 1H, styrenyl-H_o, $^4J_{HH}$ = 2,9 Hz); 7.09−7.00 (m, 2H, styrenyl-H_p, C*H*CH_2); 6.91 (d, 1H, styrenyl-H_m, $^3J_{HH}$ = 8.8 Hz); 5.71 (dd, 1H, CHCH_2(trans), $^3J_{HH}$ = 17.9 Hz, $^2J_{HH}$ = 1.3 Hz); 5.26 (dd, 1H, CHCH_2(cis), $^3J_{HH}$ = 11.3 Hz, $^2J_{HH}$ = 1.3 Hz); 4.51 (sept, 1H, C*H*Me_2, $^3J_{HH}$ = 6.1 Hz); 1.36 (d, 6H, CH*Me*$_2$, $^3J_{HH}$ = 6.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 165.5 (*C*OO); 152.9 (OC_{ipso}); 144.5 (COOC_{ipso}); 133.5, 131.3, 130.1, 129.7, 129.1, 128.5, 121.5, 119.3, 115.1, 114.8 (CAr, CH*C*H_2, *C*HCH_2); 71.6 (*C*HMe_2); 22.2 (CH*Me*$_2$). Elemental analysis (%) calcd for $C_{18}H_{18}O_3$ (282.33): C 76.57, H 6.43; found: C 76.05, H 6.50.

Terephthalic Acid Bis(4-(2-propoxy)-3-vinylphenyl) Ester (2). To a stirred solution of 5-hydroxy-2-(2-propoxy)styrene (287.9 mg, 1.62 mmol) in THF (8 mL) was added terephthaloyl chloride (163.8 mg, 0.81 mmol), dissolved in THF (1 mL). Finally, NEt_3 (163.5 mg, 1.62 mmol) was added. After stirring for 19 h at room temperature, the white reaction mixture was diluted with water (50 mL). The mixture was extracted with diethyl ether (4 × 30 mL), the combined organic extracts were washed with water (50 mL), and the solvent was evaporated under reduced pressure. The resultant material was dissolved in dichloromethane, rotated onto silica, and purified by column chromatography (silica 60: hexane: ethyl acetate 10:1, $R_f = 0.3$). Evaporation of the solvent gave **2** as a white solid (290.0 mg, 0.60 mmol, 74%). IR (ATR mode, cm^{-1}): 3084 (w); 2977 (m); 2906 (m); 1837 (w); 1728 (s); 1615 (w); 1478 (s); 1417 (m); 1376 (m); 1304 (w); 1241 (s); 1186 (s); 1164 (s); 1107 (m); 1066 (s); 1002 (s); 954 (m); 913 (s); 882 (m); 848 (m); 794 (m); 764 (m); 717 (s). ^{1}H NMR ($CDCl_3$): δ = 8.32 (s, 4H, terephthaloyl-*H*); 7.34 (d, 2H, styrenyl-H_o, $^4J_{HH}$ = 2.8 Hz); 7.07 (dd, 2H, styrenyl-H_p, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.8 Hz); 7.05 (dd, 2H, C*H*CH_2, $^3J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 11.2 Hz); 6.92 (d, 2H, styrenyl-H_m, $^3J_{HH}$ = 9.0 Hz); 5.73 (dd, 2H, CHCH_2(trans), $^3J_{HH}$ = 17.9 Hz, $^2J_{HH}$ = 1.3 Hz); 5.28 (dd, 2H, CHCH_2(cis), $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 1.3 Hz); 4.53 (sept, 2H, C*H*Me_2, $^3J_{HH}$ = 6.0 Hz); 1.37 (d, 12H, CH*Me*$_2$, $^3J_{HH}$ = 6.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 164.6 (*C*OO); 153.1 (OC_{ipso}); 144.2 (COOC_{ipso}); 134.0, 131.2, 130.2, 129.2, 121.3, 119.1, 115.1, 115.0 (CAr, CH*C*H_2, *C*HCH_2); 71.6 (*C*HMe_2); 22.2 (CH*Me*$_2$). Elemental analysis (%) calcd for $C_{30}H_{30}O_6$ (486.56): C 74.06, H 6.21; found: C 73.69, H 6.32.

Bis(4-(2-propoxy)-3-vinyl-phenoxy)diphenylsilane (3). To a stirred solution of 5-hydroxy-2-(2-propoxy)styrene (493.4 mg, 2.77 mmol) in THF (14 mL) was added dichlorodiphenylsilane (343.5 mg, 1.36 mmol) in THF (1.5 mL). Finally, NEt_3 (280.1 mg, 2.77 mmol) was added. After stirring for 19 h at room temperature, the white reaction mixture was filtered over a short pad of Celite. The solvent was removed, and the resultant oil was flashed over alumina (neutral, 6% w/w water: hexane:ethyl acetate 7:3, R_f = 0.9). Evaporation of the solvent afforded **3** as a white solid (546.5 mg, 1.02 mmol, 75%). IR (ATR mode, cm^{-1}): 3049 (w); 2973 (m); 2928 (w); 2870 (w); 1826 (w); 1621 (w); 1574 (m); 1481 (s); 1425 (m); 1377 (m); 1336 (w); 1283 (m); 1205 (s); 1179 (m); 1139 (w); 1113 (s); 1055 (m); 974 (m); 952 (s); 912 (m); 874 (m); 841 (w); 805 (m); 743 (w); 721 (m); 697 (s). ^{1}H NMR ($CDCl_3$): δ = 7.77 (m, 4H, Ph-H_o); 7.49−7.34 (m, 6H, Ph-$H_{m,p}$); 7.06 (d, 2H, styrenyl-H_o, $^4J_{HH}$ = 2.9 Hz); 6.93 (dd, 2H, C*H*CH_2, $^3J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 11.1 Hz); 6.77 (dd, 2H, styrenyl-H_p, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.9 Hz); 6.66 (d, 2H, styrenyl-H_m, $^3J_{HH}$ = 8.9 Hz); 5.45 (dd, 2H, CHCH_2(trans), $^3J_{HH}$ = 17.9 Hz, $^2J_{HH}$ = 1.4 Hz); 5.12 (dd, 2H, CHCH_2(cis), $^3J_{HH}$ = 11.1 Hz, $^2J_{HH}$ = 1.4 Hz); 4.34 (sept, 2H, C*H*Me_2, $^3J_{HH}$ = 6.2 Hz); 1.27 (d, 12H, CH*Me*$_2$, $^3J_{HH}$ = 6.2 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 150.2, 147.9 (OC_{ipso}, SiOC_{ipso}); 135.0, 131.7, 131.5, 130.8, 129.1, 128.0 (Ph-*C*, *C*CHCH$_2$, C*C*HCH$_2$); 119.6, 117.1, 116.2, 114.1 (styrenyl-$C_{o,m,p}$, CCH*C*H$_2$); 71.9 (*C*HMe_2); 22.2 (CH*Me*$_2$). Elemental analysis (%) calcd for $C_{34}H_{36}O_4Si$ (536.73): C 76.08, H 6.76; found: C 76.00, H 6.78.

Benzene-1,3,5-Tricarboxylic Acid Tris(4-(2-propoxy)-3-vinylphenyl) Ester (4). Benzene-1,3,5-tricarboxylic acid tris(4-(2-propoxy)-3-vinylphenyl) ester was prepared according to the procedure described for **2**. 5-Hydroxy-2-(2-propoxy)styrene (240.7 mg, 1.35 mmol), trimesoyl trichloride (119.2 mg, 0.45 mmol), THF (8 mL), and NEt_3 (136.7 mg, 1.35 mmol) were used. Stirring for 12 h at room temperature, dilution with water (40 mL), extraction with diethyl ether (4 × 20 mL), washing with water, and evaporation of the solvent afforded the crude product which was dissolved in dichloromethane, rotated onto silica, and purified by column chromatography (silica 60: hexane:ethyl acetate 10:1, R_f = 0.2). Removal of the solvent under reduced pressure yielded **4** as a white solid (250.0 mg, 0.36 mmol, 81%). IR (ATR mode, cm^{-1}): 3083 (w); 2976 (m); 2929 (w); 1849 (w); 1735 (s); 1620 (w); 1483 (m); 1426 (m); 1377 (m); 1270 (w); 1207 (vs); 1104 (s); 993 (m); 916 (s); 855 (m); 809 (s); 768 (m); 725 (s). ^{1}H NMR ($CDCl_3$): δ = 9.21 (s, 3H, trimesoyl-*H*); 7.36 (d, 3H, styrenyl-H_o, $^4J_{HH}$ = 2.8 Hz); 7.09 (dd, 3H, styrenyl-H_p, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.8 Hz); 7.05 (dd, 3H, C*H*CH_2, $^3J_{HH}$ = 17.8 Hz, $^3J_{HH}$ = 11.2 Hz); 6.93 (d, 3H, styrenyl-H_m, $^3J_{HH}$ = 9.0 Hz); 5.73 (dd, 3H, CHCH_2(trans), $^3J_{HH}$ = 17.8 Hz, $^2J_{HH}$ = 1.3 Hz); 5.28 (dd, 3H, CHCH_2(cis), $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 1.3 Hz); 4.53 (sept, 3H, C*H*Me_2, $^3J_{HH}$ = 6.0 Hz); 1.37 (d, 18H, CH*Me*$_2$, $^3J_{HH}$ = 6.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 163.7 (*C*OO); 153.2 (OC_{ipso}); 144.1 (COOC_{ipso}); 135.9, 131.3, 131.2, 131.1, 129.2, 121.2, 119.1, 115.0 (*C*Ar, CH*C*H_2, *C*HCH_2); 71.6 (*C*HMe_2); 22.2 (CH*Me*$_2$). Elemental analysis (%) calcd for $C_{42}H_{42}O_9$ (690.78): C 73.03, H 6.13; found: C 72.77, H 6.26.

$RuCl_2(IMesH_2)$(=CH-2-(2-PrO)-C_6H_3-5-$OOCC_6H_5$) (I1a). Under drybox conditions, **1** (29.8 mg, 0.106 mmol) was dissolved in CH_2Cl_2 (1 mL), and the solution was added to a vigorously stirred solution of $RuCl_2(IMesH_2)(PCy_3)$(=CHPh) (94.2 mg, 0.111 mmol) in CH_2Cl_2 (6 mL). After a few minutes, excess CuCl (∼50 mg) was added to the red-purple solution. The color of the reaction mixture changed to green-brown when heated to reflux for 1 h. Evaporation of the solvent and purification by column chromatography (silica 60: CH_2Cl_2:pentane 1:1 → 3:1, R_f (3:1) = 0.4) afforded **I1a** as a bright green solid (57.3 mg, 0.077 mmol, 73%). IR (ATR mode, cm^{-1}): 2980 (w); 2959 (w); 2918 (m); 2852 (w); 1736 (s); 1600 (w); 1479 (s); 1445 (m); 1423 (m); 1393 (m); 1377 (m); 1312 (w); 1241 (s); 1209 (s); 1177 (m); 1131 (m); 1102 (m); 1075 (w); 1055 (s); 1021 (m); 928 (m); 897 (m); 852 (m); 804 (w); 708 (s). ^{1}H NMR ($CDCl_3$): δ = 16.51 (s, 1H, RuC*H*R); 8.18 (m, 2H, Ph-H_o); 7.64 (m, 1H, Ph-H_p); 7.51 (m, 2H, Ph-H_m); 7.37 (dd, 1H, benzylidene-H_p, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.7 Hz); 7.07 (s, 4H, Mes-*H*); 6.81 (m, 2H, benzylidene-$H_{o,m}$); 4.89 (sept, 1H, C*H*Me_2, $^3J_{HH}$ = 6.1 Hz); 4.16 (s, 4H, CH_2CH_2); 2.47 (s, 12H, *o*-CH_3Mes); 2.37 (s, 6H, *p*-CH_3Mes); 1.28 (d, 6H, CH*Me*$_2$, $^3J_{HH}$ = 6.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 294.2 (Ru*C*HR); 210.4 (Ru*C*$(N)_2$); 165.3 (*C*OO); 149.6, 146.0, 145.5, 139.0, 138.8, 133.5, 130.1, 129.4, 129.3, 128.6, 128.5, 121.7, 114.8, 113.0 (*C*Ar); 75.6 (*C*HMe_2); 51.5 (CH_2CH_2); 22.0, 21.1, 19.4 (CH*Me*$_2$, *o*-CH_3Mes, *p*-CH_3Mes). Elemental analysis (%) calcd for $C_{38}H_{42}Cl_2N_2O_3Ru$ (746.73): C 61.12, H 5.67, N 3.75; found: C 60.84, H 5.51, N 3.64.

$Ru(OOCCF_3)_2(IMesH_2)$(=CH-2-(2-PrO)-C_6H_3-5-$OOCC_6H_5$) (I1b). Under drybox conditions, **I1a** (34.3 mg, 0.046 mmol) was dissolved in THF (11 mL), and a solution of CF_3COOAg (20.7 mg, 0.094 mmol) in THF (1 mL) was slowly added. Stirring was continued for 5 h at room temperature in the absence of light. The reaction mixture was centrifuged, the precipitate was filtered off, and the violet solution was evaporated to dryness, yielding **I1b** as a violet solid (40.5 mg, 0.045 mmol, 98%). IR (ATR mode, cm^{-1}):

2960 (w); 2921 (m); 2859 (w); 1966 (w); 1691 (m); 1603 (w); 1482 (m); 1430 (m); 1392 (m); 1313 (w); 1258 (m); 1179 (s); 1136 (s); 1058 (m); 1023 (m); 927 (m); 897 (w); 846 (m); 808 (m); 753 (w); 711 (m). ^{1}H NMR ($CDCl_3$): δ = 17.45 (s, 1H, RuC*H*R); 8.16 (pseudo-*d*, 2H, Ph-H_o, $^3J_{HH}$ = 7.3 Hz); 7.63 (m, 1H, Ph-H_p); 7.51 (m, 2H, Ph-H_m); 7.32 (dd, 1H, benzylidene-H_p, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.5 Hz); 7.15 (s, 4H, Mes-*H*); 6.96 (d, 1H, benzylidene-H_o, $^4J_{HH}$ = 2.5 Hz); 6.66 (d, 1H, benzylidene-H_m, $^3J_{HH}$ = 9.0 Hz); 4.61 (sept, 1H, C*H*Me$_2$, $^3J_{HH}$ = 6.0 Hz); 4.12 (s, 4H, CH_2CH$_2$); 2.42 (s, 6H, *p*-CH_3Mes); 2.27 (s, 12H, *o*-CH_3Mes); 0.96 (d, 6H, CH*Me*$_2$, $^3J_{HH}$ = 6.0 Hz).^{13}C{^{1}H} NMR ($CDCl_3$): δ = 313.8 (Ru*C*HR); 209.2 (Ru*C*(N)$_2$); 164.8 (*C*OO); 160.3 (q, CF$_3$*C*OO, $^2J_{CF}$ = 36 Hz); 150.5, 146.1, 143.8, 139.6, 138.8, 134.3, 133.4, 130.1, 129.8, 129.7, 128.5, 122.6, 115.8 (*C*Ar); 114.2 (q, *C*F$_3$COO, $^1J_{CF}$ = 290 Hz); 111.1 (*C*Ar); 74.9 (*C*HMe$_2$); 51.4 (*C*H$_2$CH$_2$); 21.1, 20.2, 17.8 (CH*Me*$_2$, *o*-*C*H$_3$Mes, *p*-*C*H$_3$Mes). ESI-MS calcd. for $C_{42}H_{42}F_6N_2O_7Ru$: 902.19, found: *m*/*z* (%) 789.0 (11) [M − CF$_3$COO]$^+$; 675.3 (81) [M − 2CF$_3$COOH + H]$^+$; 633.3 (79) [M − 2CF$_3$COOH − C$_3$H$_6$ + H]$^+$; 571.3 (30) [M − 2CF$_3$COO − C$_6$H$_5$CO]$^+$; 486.8 (95) [M − benzylidene − CH$_2$NMes]$^+$.

1,4-[RuCl$_2$(IMesH$_2$)(═CH-2-*i*PrO−C$_6$H$_3$-5-OOC)]$_2$C$_6$H$_4$ (I2a). Under drybox conditions, **2** (106.0 mg, 0.218 mmol) dissolved in CH_2Cl_2 (2 mL) was added to a vigorously stirred solution of RuCl$_2$(IMesH$_2$)(PCy$_3$)(═CHPh) (381.0 mg, 0.449 mmol) in CH_2Cl_2 (38 mL). After a few minutes, excess CuCl (∼150 mg) was added to the red-purple solution. The color of the reaction mixture changed to green-brown when heated to reflux for 1 h. Evaporation of the solvent and purification by column chromatography (silica 60: dichloromethane:hexane 2:1 → 4:1, $R_f \ll 0.1$; dichloromethane: ethyl acetate 10:1, R_f = 0.9) afforded **I2a** as a green solid (195.0 mg, 0.138 mmol, 63%). IR (ATR mode, cm^{-1}): 2956 (w); 2920 (m); 2853 (w); 1740 (m); 1602 (w); 1477 (m); 1444 (m); 1422 (m); 1385 (m); 1300 (w); 1242 (s); 1209 (m); 1177 (m); 1133 (m); 1098 (m); 1065 (s); 1035 (w); 1013 (m); 926 (m); 893 (m); 850 (m); 801 (m); 720(m). ^{1}H NMR ($CDCl_3$): δ = 16.51 (s, 2H, RuC*H*R); 8.31 (s, 4H, terephthaloyl-*H*); 7.40 (dd, 2H, benzylidene-H_p, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.8 Hz); 7.07 (s, 8H, Mes-*H*); 6.83 (m, 4H, benzylidene-$H_{o,m}$); 4.89 (sept, 2H, C*H*Me$_2$, $^3J_{HH}$ = 6.0 Hz); 4.17 (s, 8H, CH_2CH$_2$); 2.47 (s, 24H, *o*-CH_3Mes); 2.38 (s, 12H, *p*-CH_3Mes); 1.29 (d, 12H, CH*Me*$_2$, $^3J_{HH}$ = 6.0 Hz). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 293.8 (Ru*C*HR); 210.3 (Ru*C*(N)$_2$); 164.4 (*C*OO); 149.7, 145.8, 145.6, 139.0, 138.9, 133.8, 130.3, 129.4, 121.4, 115.2, 114.6, 113.1 (*C*Ar); 75.7 (*C*HMe$_2$); 51.5 (*C*H$_2$CH$_2$); 22.0, 21.1, 19.4 (CH*Me*$_2$, *o*-*C*H$_3$Mes, *p*-*C*H$_3$Mes). Elemental analysis (%) calcd for $C_{70}H_{78}Cl_4N_4O_6Ru_2$ (1415.34): C 59.40, H 5.55, N 3.96; found: C 59.04, H 5.68, N 3.68.

1,4-[Ru(OOCCF$_3$)$_2$(IMesH$_2$)(═CH-2-*i*PrO-C$_6$H$_3$-5-OOC)]$_2$-C$_6$H$_4$ (I2b). Under drybox conditions, **I2a** (101.8 mg, 0.072 mmol) was dissolved in THF (19 mL), and a solution of CF_3COOAg (64.5 mg, 0.292 mmol) in THF (1 mL) was slowly added. Stirring was continued for 5 h at room temperature in the absence of light, the precipitate formed was filtered off, and the violet solution was evaporated to dryness. The crude product was purified by filtration over a short plug of alumina (CH_2Cl_2:hexane 4:1), and the solvent was removed in vacuo, yielding **I2b** as a violet solid (111.8 mg, 0.065 mmol, 90%). IR (ATR mode, cm^{-1}): 2957 (w); 2922 (m); 2855 (w); 1737 (m); 1696 (m); 1648 (m); 1607 (w); 1482 (m); 1432 (m); 1395 (m); 1313 (w); 1260 (m); 1245 (m); 1181 (s); 1137 (s); 1101 (w); 1069 (m); 1016 (m); 926 (m);897 (w); 845 (m); 803 (m); 719 (m). ^{1}H NMR ($CDCl_3$): δ 17.45 (s, 2H, RuC*H*R); 8.28 (s, 4H, terephthaloyl-*H*); 7.37 (dd, 2H, benzylidene-H_p, $^3J_{HH}$ = 9.1 Hz, $^4J_{HH}$ = 2.3 Hz); 7.16 (s, 8H, Mes-*H*); 7.01 (d, 2H, benzylidene-H_o, $^4J_{HH}$ = 2.3 Hz); 6.68 (d, 2H, benzylidene-H_m, $^3J_{HH}$ = 9.1 Hz); 4.63 (sept, 2H, C*H*Me$_2$, $^3J_{HH}$ = 5.5 Hz); 4.13 (s, 8H, CH_2CH$_2$); 2.44 (s, 12H, *p*-CH_3Mes); 2.27 (s, 24H, *o*-CH_3Mes); 0.97 (d, 12H, CH*Me*$_2$, $^3J_{HH}$ = 5.5 Hz).^{13}C{^{1}H} NMR ($CDCl_3$): δ = 313.6 (Ru*C*HR); 209.0 (Ru*C*(N)$_2$); 163.8 (*C*OO); 160.3 (q, CF$_3$*C*OO, $^2J_{CF}$ = 36 Hz); 150.6, 145.9, 143.7, 139.6, 138.8, 134.2, 133.9, 130.2, 129.8, 122.3, 115.6 (*C*Ar); 114.1 (q, *C*F$_3$COO, $^1J_{CF}$ = 291 Hz); 111.1 (*C*Ar); 75.0 (*C*HMe$_2$); 51.3 (*C*H$_2$CH$_2$); 21.2, 20.1, 17.8 (CH*Me*$_2$, *o*-*C*H$_3$Mes, *p*-*C*H$_3$Mes). ESI-MS calcd for $C_{78}H_{78}F_{12}N_4O_{14}Ru_2$: 1726.34; found: *m*/*z* (%) 1694.8 (24) [M − 2CH$_4$ + H]$^+$; 1500.0 (12) [M − 2CF$_3$COO]$^+$; 881.3 (53) [M − 2CF$_3$COO − Ru(IMesH$_2$)(═CH-2-(2-PrO)-C$_6$H$_3$-5-OOC) − HF]$^+$; 825.4 (54) [M − 2CF$_3$COO − Ru(IMesH$_2$)(═CH-2-(2-PrO)-C$_6$H$_3$-5-OOCC$_6$H$_4$)]$^+$; 571.4 (18) [M − 4CF$_3$COO − Ru(IMesH$_2$)(═CH-2-(2-PrO)-C$_6$H$_3$-5-OOCC$_6$H$_4$CO)]$^+$; 486.9 (94) [M − benzylidene − CH$_2$NMes]$^+$.

[RuCl$_2$(IMesH$_2$)(═CH-2-*i*PrO−C$_6$H$_3$-5-O)]$_2$SiPh$_2$ (I3a). Under drybox conditions, **3** (26.9 mg, 0.050 mmol) dissolved in dichloromethane (1 mL) was added to a vigorously stirred solution of RuCl$_2$-(IMesH$_2$)(PCy$_3$)(═CHPh) (87.7 mg, 0.103 mmol) in CH_2Cl_2 (6 mL). After a few minutes, excess CuCl (∼60 mg) was added to the red-purple solution. The color of the reaction mixture changed to green-black when heated to reflux for 45 min. The solvent was removed, and the resultant material was purified by column chromatography (neutral alumina, 6% w/w water:CH_2Cl_2). Evaporation of the solvent and precipitation from dichloromethane/pentane gave **I3a** as a bright green solid (30.8 mg, 0.021 mmol, 42%). IR (ATR mode, cm^{-1}): 2970 (w); 2957 (w); 2918 (m); 2852 (w); 1598 (w); 1578 (w); 1482 (s); 1448(w); 1420 (m); 1379 (w); 1257 (s); 1211 (m); 1192 (m); 1123 (m); 1106 (m); 1030 (w); 985 (m); 937 (m); 887 (m); 873 (m); 850 (m); 813 (m); 759 (w); 742 (w); 719 (m); 696 (s). ^{1}H NMR ($CDCl_3$): δ = 16.36 (s, 2H, RuC*H*R); 7.66 (m, 4H, Ph-H_o); 7.49−7.35 (m, 6H, Ph-$H_{m,p}$); 7.05 (dd, 2H, benzylidene-H_p, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.7 Hz); 6.99 (s, 8H, Mes-*H*); 6.55 (d, 2H, benzylidene-H_m, $^3J_{HH}$ = 8.9 Hz); 6.54 (d, 2H, benzylidene-H_o, $^4J_{HH}$ = 2.7 Hz); 4.75 (sept, 2H, C*H*Me$_2$, $^3J_{HH}$ = 6.0 Hz); 4.13 (s, 8H, CH_2CH$_2$); 2.42 (s, 24H, *o*-CH_3Mes); 2.31 (s, 12H, *p*-CH_3Mes); 1.19 (d, 12H, CH*Me*$_2$, $^3J_{HH}$ = 6.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 295.8 (Ru*C*HR); 211.2 (Ru*C*(N)$_2$); 149.0, 147.2, 145.7, 138.8, 135.0, 130.9, 130.8, 129.3, 128.6, 128.1, 126.5, 119.6, 113.0, 112.7 (*C*Ar); 74.9 (*C*HMe$_2$); 51.5 (*C*H$_2$CH$_2$); 22.2, 21.1, 19.3 (CH*Me*$_2$, *o*-*C*H$_3$Mes, *p*-*C*H$_3$Mes). Elemental analysis (%) calcd for $C_{74}H_{84}Cl_4N_4O_4Ru_2Si$ (1465.52): C 60.65, H 5.78, N 3.82; found: C 60.50, H 5.67, N 3.35.

[Ru(OOCCF$_3$)$_2$(IMesH$_2$)(═CH-2-*i*PrO−C$_6$H$_3$-5-O)]$_2$SiPh$_2$ (I3b). Under drybox conditions, **I3a** (89.4 mg, 0.061 mmol) was dissolved in THF (23 mL), and a solution of CF_3COOAg (54.7 mg, 0.248 mmol) in THF (1 mL) was slowly added. Stirring was continued for 3 h at room temperature in the absence of light, the precipitate formed was filtered off, and the gray-brown solution was evaporated to dryness. The crude product was purified by filtration over a short plug of alumina (dichloromethane), and the solvent was removed in vacuo, yielding **I3b** as a brown-violet solid (106.6 mg, 0.060 mmol, 98%). IR (ATR mode, cm^{-1}): 2924 (m); 2853 (w); 1698 (s); 1589 (w); 1483 (s); 1446 (m); 1426 (m); 1392 (m); 1259 (s); 1180 (s); 1134 (s); 1031 (w); 982 (m); 938 (m); 888 (m); 875 (m); 845 (m); 800 (m); 784 (w);762 (w), 744 (w); 720 (s); 697 (s). ^{1}H NMR ($CDCl_3$): δ = 17.28 (s, 2H, RuC*H*R); 7.67 (m, 4H, Ph-H_o); 7.49−7.36 (m, 6H, Ph-$H_{m,p}$); 7.08 (s, 8H, Mes-*H*); 6.76 (dd, 2H, benzylidene-H_p, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.9 Hz); 6.64 (d, 2H, benzylidene-H_o, $^4J_{HH}$ = 2.9 Hz); 6.34 (d, 2H, benzylidene-H_m, $^3J_{HH}$ = 8.8 Hz); 4.41 (sept, 2H, C*H*Me$_2$, $^3J_{HH}$ = 6.1 Hz); 4.09 (s, 8H, CH_2CH$_2$); 2.36 (s, 12H, *p*-CH_3Mes); 2.24 (s, 24H, *o*-CH_3Mes); 0.85 (d, 12H, CH*Me*$_2$, $^3J_{HH}$ = 6.1 Hz). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 315.0 (Ru*C*HR); 210.1 (Ru*C*(N)$_2$); 160.2 (q, CF$_3$*C*OO, $^2J_{CF}$ = 36 Hz); 149.0, 148.2, 143.6, 139.4, 138.7, 135.0, 134.4, 131.4, 130.8, 129.7, 128.1, 121.0, 114.3 (*C*Ar); 114.2 (q, *C*F$_3$COO, $^1J_{CF}$ = 290 Hz); 111.4 (*C*Ar); 74.2 (*C*HMe$_2$); 51.3 (*C*H$_2$CH$_2$); 21.0, 20.0, 17.7 (CH*Me*$_2$, *o*-*C*H$_3$Mes, *p*-*C*H$_3$Mes). ESI-MS calcd for $C_{82}H_{84}F_{12}N_4O_{12}Ru_2Si$: 1776.38, found: *m*/*z* (%) 1549.1 (23) [M − 2CF$_3$COOH + H]$^+$; 917.4 (41) [M − 2CF$_3$COOH − Ru(IMesH$_2$)(═CH-2-(2-PrO)-C$_6$H$_3$) − C$_6$H$_5$ + H]$^+$; 571.3 (10) [M − 4CF$_3$COO − Ru(IMesH$_2$)(═CH-2-(2-PrO)-C$_6$H$_3$-5-OSiPh$_2$)]$^+$; 486.8 (100) [M − benzylidene − CH$_2$NMes]$^+$.

1,3,5-[RuCl$_2$(IMesH$_2$)(═CH-2-*i*PrO−C$_6$H$_3$-5-OOC)]$_3$C$_6$H$_3$ (I4a). Under drybox conditions, **4** (119.3 mg, 0.173 mmol) dissolved in CH_2Cl_2 (2 mL) was added to a vigorously stirred solution of RuCl$_2$-(IMesH$_2$)(PCy$_3$)(═CHPh) (448.8 mg, 0.529 mmol) in CH_2Cl_2 (58 mL). After a few minutes, excess CuCl (∼190 mg) was added to the red-purple solution. The color of the reaction mixture changed

to green-brown when heated to reflux for 1 h. Evaporation of the solvent and purification by column chromatography (silica 60: CH_2Cl_2:hexane 4:1 → 8:1, $R_f \ll 0.1$; CH_2Cl_2:ethyl acetate 10:1, $R_f = 0.9$) afforded **I4a** as a green solid (154.7 mg, 0.074 mmol, 43%). IR (ATR mode, cm^{-1}): 3081 (w); 2955 (w); 2910 (m); 2852 (w); 1742 (s); 1599 (w); 1479 (s); 1425 (m); 1386 (m); 1260 (s); 1196 (vs); 1136 (s); 1097 (s); 1029 (m); 972 (w); 926 (m); 852 (m); 810 (m); 720 (m). ^1H NMR ($CDCl_3$): $\delta = 16.55$ (s, 3H, RuC*H*R); 9.17 (s, 3H, trimesoyl-*H*); 7.45 (dd, 3H, benzylidene-H_p, $^3J_{HH} = 8.9$ Hz, $^4J_{HH} = 2.7$ Hz); 7.07 (s, 12H, Mes-*H*); 6.89 (d, 3H, benzylidene-H_o, $^4J_{HH} = 2.7$ Hz); 6.85 (d, 3H, benzylidene-H_m, $^3J_{HH} = 8.9$ Hz); 4.91 (sept, 3H, C*H*Me$_2$, $^3J_{HH} = 6.0$ Hz); 4.17 (s, 12H, CH_2CH$_2$); 2.48 (s, 36H, *o*-CH_3Mes); 2.38 (s, 18H, *p*-CH_3Mes); 1.30 (d, 18H, CH*Me*$_2$, $^3J_{HH} = 6.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 293.8$ (Ru*C*HR); 210.2 (Ru*C*(N)$_2$); 163.5 (*C*OO); 149.8, 145.7, 145.5, 139.1, 138.9, 136.1, 136.0, 131.1, 129.4, 121.2, 114.5, 113.1 (*C*Ar); 75.8 (*C*HMe$_2$); 51.5 (*C*H$_2$CH$_2$); 22.0, 21.1, 19.3 (CH*Me*$_2$, *o*-*C*H$_3$Mes, *p*-*C*H$_3$Mes). Elemental analysis (%) calcd for $C_{102}H_{114}Cl_6N_6O_9Ru_3$ (2083.96): C 58.79, H 5.51, N 4.03; found: C 58.93, H 5.38, N 3.74.

1,3,5-[Ru(OOCCF$_3$)$_2$(IMesH$_2$)(=CH-2-*i*PrO−C$_6$H$_3$-5-OOC)]$_3$C$_6$H$_3$ (I4b). Under drybox conditions, **I4a** (104.9 mg, 0.050 mmol) was dissolved in THF (15 mL), and a solution of CF_3COOAg (68.4 mg, 0.310 mmol) in THF (1 mL) was slowly added. Stirring was continued for 4 h at room temperature in the absence of light, the precipitate formed was filtered off, and the violet solution was evaporated to dryness. The crude product was purified by filtration over a short plug of alumina (CH_2Cl_2: hexane 4:1), and the solvent was removed in vacuo, yielding **I4b** as a gray-violet solid (127.5 mg, 0.050 mmol, 99%). IR (ATR mode, cm^{-1}): 2959 (w); 2920 (w); 2859 (w); 1744 (w); 1693 (m); 1605 (w); 1482 (m); 1429 (w); 1390 (m); 1314 (w); 1261 (m); 1179 (s); 1135 (s); 1096 (m); 1025 (m); 930 (m); 847 (m); 805 (m); 721 (m). ^1H NMR ($CDCl_3$): $\delta = 17.44$ (s, 3H, RuC*H*R); 9.15 (s, 3H, trimesoyl-*H*); 7.45 (dd, 3H, benzylidene-H_p, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.7$ Hz); 7.17 (s, 12H, Mes-*H*); 7.13 (d, 3H, benzylidene-H_o, $^4J_{HH} = 2.7$ Hz); 6.71 (d, 3H, benzylidene-H_m, $^3J_{HH} = 8.7$ Hz); 4.64 (sept, 3H, C*H*Me$_2$, $^3J_{HH} = 6.4$ Hz); 4.13 (s, 12H, CH_2CH$_2$); 2.43 (s, 18H, *p*-CH_3Mes); 2.27 (s, 36H, *o*-CH_3Mes); 0.98 (d, 18H, CH*Me*$_2$, $^3J_{HH} = 6.4$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 313.6$ (Ru*C*HR); 209.1 (Ru*C*(N)$_2$); 162.8 (*C*OO); 160.3 (q, CF_3COO, $^2J_{CF} = 36$ Hz); 150.6, 145.9, 143.8, 139.7, 138.8, 135.9, 134.2, 131.3, 129.8, 122.2, 115.6 (*C*Ar); 114.2 (q, *C*F$_3$COO, $^1J_{CF} = 292$ Hz); 111.2 (*C*Ar); 75.0 (*C*HMe$_2$); 51.4 (*C*H$_2$CH$_2$); 21.2, 20.2, 17.8 (CH*Me*$_2$, *o*-*C*H$_3$Mes, *p*-*C*H$_3$Mes). ESI-MS calcd for $C_{114}H_{114}F_{18}N_6O_{21}Ru_3$: 2550.49; found: *m*/*z* (%) 571.2 (12) [M − 6CF$_3$COO − (Ru(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_3$-5-OOC)$_2$C$_6$H$_3$CO)]$^+$; 486.9 (100) [M − benzylidene − CH$_2$NMes]$^+$.

Synthesis of A$_n$−X−A$_n$ Type Block and (A$_n$)$_3$X Type Tristar Copolymers of M1−M4 and M6 Using I1a−I4a and I1b−I4b. A solution of the monomer in CH_2Cl_2 (0.3 mL) was added to the solution of the initiator in CH_2Cl_2 ([Ru] ca. 0.9 mmol Ru/L) under vigorous stirring. After 3−4 h (**M1**, **M5**), 24 h (**M2**, **M3**), and 3−5 h (**M4**) at room temperature, excess ethyl vinyl ether was added, and the red to violet reaction mixture was stirred for another 30 min. The solvent was removed in vacuo, methanol (∼10 mL) was added to the residue, and stirring was continued for 30 min after sonification. The product was centrifuged and dried in vacuo to yield a dark solid. Representative analytic data are given in the following:

Poly-M2$_{50}$ Prepared Using Either I1b, I2b, I3b, or I4b. IR (ATR mode, cm^{-1}): 2977 (m); 2933 (w); 2905 (w); 2863 (w); 1722 (s); 1444 (m); 1387 (w); 1366 (m); 1244 (s); 1178 (s); 1159 (s); 1096 (m); 1055 (s); 1009 (m); 947 (s); 900 (w); 860 (m); 816 (w); 698 (m). ^1H NMR ($CDCl_3$): $\delta = 7.10-6.30$ (br m, 2H, $H_{olefinic}$); 4.26 (br m, 4H, OCH_2Me); 3.42 (br m, 4H, C$H_{2allylic}$); 1.28 (br m, 6H, OCH$_2$*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 171.5$ (*C*OO); 136.5, 122.7 ($C_{olefinic}$); 61.5 (OCH_2Me); 56.8 (C_{ipso}); 41.0 ($C_{allylic}$); 13.7 (OCH$_2$*Me*).

Poly-M3$_{70}$ Prepared Using I2b. IR (ATR mode, cm^{-1}): 2973 (m); 2930 (w); 1724 (s); 1480 (w); 1367 (m); 1286 (m); 1257 (s); 1171 (s); 1139 (s); 1101 (s); 1069 (s); 1017 (s); 949 (w); 847 (m); 798 (s). ^1H NMR ($CDCl_3$): $\delta = 7.10-6.40$ (br m, 2H, $H_{olefinic}$); 3.31 (br m, 4H, C$H_{2allylic}$); 1.49 (br m, 18H, C*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 170.7$ (*C*OO); 136.5, 122.7 ($C_{olefinic}$); 81.0 (*C*Me$_3$); 57.7 (C_{ipso}); 40.8 ($C_{allylic}$); 27.4 (C*Me*$_3$).

Poly-M4$_{70}$ Prepared Using Either I2b or I4b. IR (ATR mode, cm^{-1}): 3040 (w); 2980 (m); 2903 (m); 2846 (w); 1725 (s); 1445 (w); 1373 (m); 1343 (w); 1304 (w); 1261 (m); 1202 (s); 1158 (s); 1096 (m); 1034 (s); 941 (m); 861 (w); 802 (w). ^1H NMR ($CDCl_3$): $\delta = 7.00-6.20$ (br m, 2H, $H_{olefinic}$); 4.20 (br m, 2H, OCH_2Me); 3.30−2.30 (br m, 5H, C$H_{2allylic}$, C*H*COOEt); 1.25 (br m, 3H, OCH$_2$*Me*). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 175.2$ (*C*OO); 137.7, 122.6 ($C_{olefinic}$); 60.4 (OCH$_2$Me); 39.7 (*C*HCOOEt); 36.7 ($C_{allylic}$); 13.9 (OCH$_2$*Me*).

Cyclopolymerizations of M5. A solution of the monomer in methanol (0.3 mL) was added to the solution of the initiator in a mixture of CH_2Cl_2 and methanol ([Ru] ca. 0.9 mmol Ru/L) all at once under vigorous stirring. The overall ratio of CH_2Cl_2/methanol was 2:1 after the monomer solution was supplied. The color changed to red and finally to violet. After 3 h at room temperature, excess ethyl vinyl ether was added, and purple poly-**M5** was isolated following the procedure described for the cyclopolymerizations of **M1**−**M4** and **M6** using ruthenium-based initiators.

Cleavage of Siloxane-Bridged M2$_{25}$-CH-[2-(2-PrO)-1,5-C$_6$H$_3$]-O-SiPh$_2$-O-[2-(2-PrO)-1,5-C$_6$H$_3$]-CH-M2$_{25}$. A sample of polymer ($M_n = 23\,300$, $M_w = 38\,700$, PDI = 1.66) prepared by the action of initiator **I3b** (1.6 mg) was dissolved in CH_2Cl_2 (0.7 mL), and TBAF (20μL, 1 M solution in THF) was added. After stirring at room temperature for 7 h, the reaction mixture was passed over a short pad of alumina, and the solution was concentrated to ∼0.5 mL under reduced pressure. Freeze-drying from benzene afforded a red-violet solid. $M_n = 11\,800$, $M_w = 17\,900$, PDI = 1.52.

Determination of the Ratio of k_p/k_i. Experiments were carried out at 300 K in chloroform-d_1 according to procedures described in the literature.[41]

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Supporting Information Available: GPC, UV−vis data, and yields for polyenes prepared using monomers **M2** and **M4** and initiators **I2b** and **I4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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