

Understanding the Origin of the Regioselectivity in Cyclopolymerizations of Diynes and How to Completely Switch It

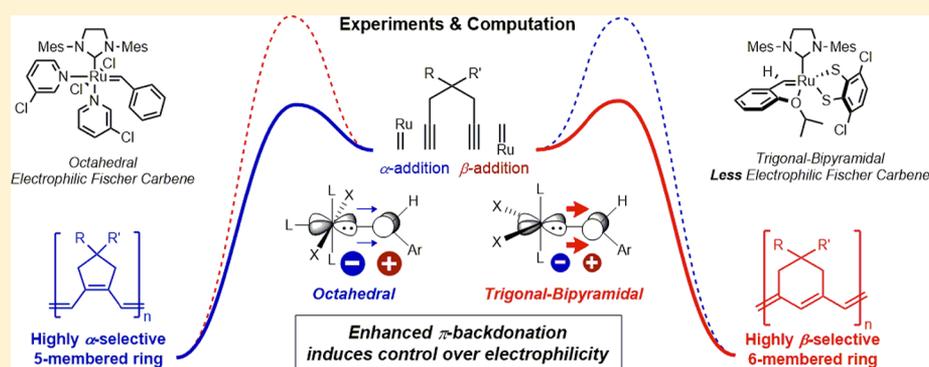
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Supporting Information



ABSTRACT: Grubbs-type olefin metathesis catalysts are known to cyclopolymerize 1,6-heptadiynes to afford conjugated polyenes containing five- or six-membered carbocycles. Although high levels of regioselectivity up to >99:1 were observed previously for the formation of five-membered rings, it was neither possible to deliberately obtain six-membered rings at similar levels of selectivity nor understood why certain catalysts showed this selectivity. Combining experimental and computational methods, a novel and general theory for what controls the regiochemistry of these cyclopolymerizations is presented. The electronic demands of the ruthenium-based Fischer carbenes are found to innately prefer to form five-membered rings. Reducing the electrophilicity of the carbene by enforcing a trigonal-bipyramidal structure for the ruthenium, where stronger π -backdonation increases the electron density on the carbene, is predicted to invert the regioselectivity. Subsequent experiments provide strong support for the new concept, and it is possible to completely switch the regioselectivity to a ratio of <1:99.

INTRODUCTION

Cyclopolymerization of diynes is a powerful and versatile method for forming conjugated polyenes, most notably soluble polyacetylenes that are difficult to access by other means. Olefin metathesis catalysts are particularly effective for producing conjugated polyenes with excellent control over molecular weight and narrow dispersity.¹ Precisely controlling the regiochemical outcome in these reactions is a major challenge, because it is difficult for the catalyst to discriminate between the α - and β -positions of a terminal alkyne substrate, such as 1,6-heptadiyne. As highlighted in Scheme 1a, the α -addition of the metal carbene to alkynes results in conjugated polymers containing five-membered rings, whereas the β -addition gives six-membered rings. In early days, catalysts showed no selectivity and produced ill-defined conjugated polymers with mixtures of five- and six-membered rings. In a pioneering effort, Schrock and co-workers² and Buchmeiser and co-workers³ showed that regioselective cyclopolymerization is possible with Mo catalysts. Subsequently, Buchmeiser and co-workers observed that 1,6-heptadiyne derivatives can be cyclopoly-

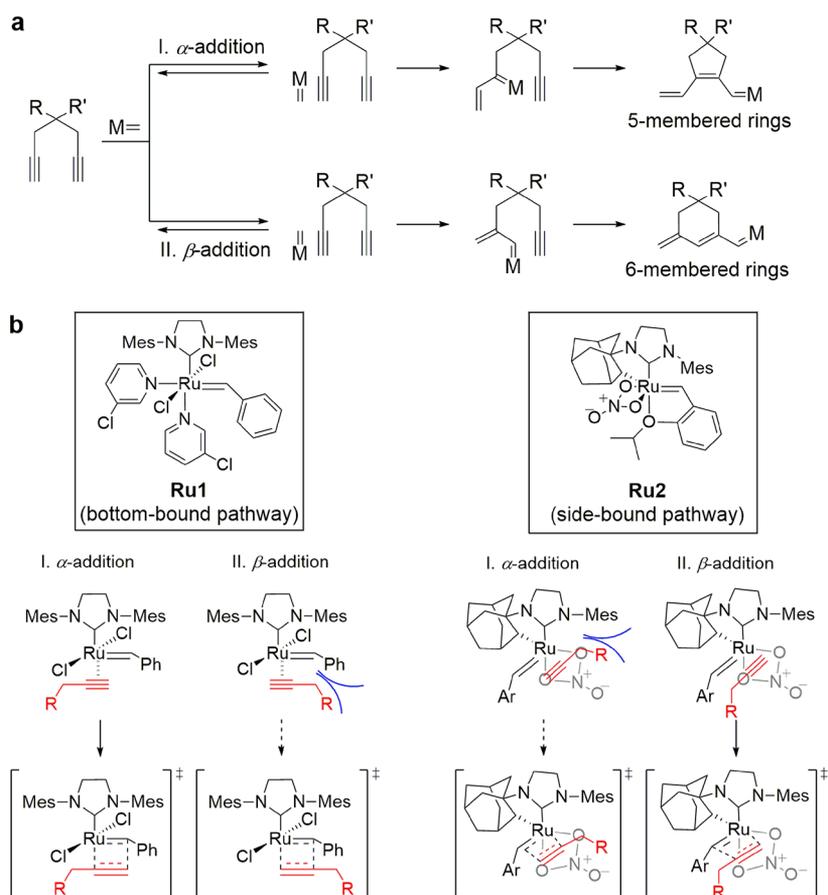
merized using a modified Grubbs' catalyst in an exclusively α -selective fashion.⁴

Recently, we reported a highly efficient living cyclopolymerization employing the third-generation Grubbs catalyst (**Ru1**)⁵ to afford conjugated polyenes consisting of five-membered rings with excellent molecular weight control and narrow dispersity.^{6–8} Interestingly, Grubbs' Z-selective catalyst (**Ru2**),⁹ which carries a chelating N-heterocyclic carbene (NHC) ligand, gave β -addition products, forming conjugated polyenes made of six-membered rings with a respectable selectivity of 70–85% at ambient conditions.¹⁰ Thus, for both the Schrock- and Grubbs-type catalysts, regiocontrol is possible. Although some attempts were made to rationalize these findings, there is currently no theory that allows for understanding and rationally enhancing the regiocontrol based on intuitive guiding principles. For example, it is unclear how the moderate regioselectivity displayed by **Ru2** may be

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Scheme 1. (a) Two Possible Pathways for the Cyclopolymerization of 1,6-Heptadiynes; (b) Bottom- and Side-Bound Models for the Cyclopolymerization



improved. For technical applications to be feasible, much higher selectivities are needed.

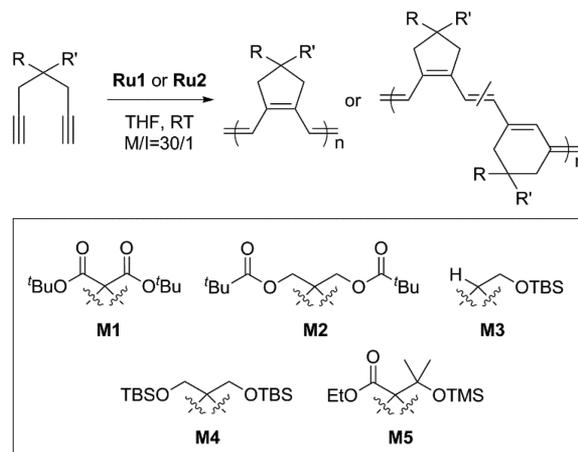
To avoid laborious trial and error explorations, we embarked on a combined experimental and computational study to establish a conceptual foundation for our optimization efforts. For the first time, we present a comprehensive and unified theory on how to exercise regiocontrol in cyclopolymerizations using ruthenium-based Fischer carbene catalysts. We demonstrate the utility of this new proposal by identifying a new cyclopolymerization process that shows an unprecedentedly high level of selectivity for β -addition.

RESULTS AND DISCUSSION

Previously, the *E/Z*-selectivity in olefin metathesis was rationalized by invoking different geometries that the Ru catalyst may adopt upon binding the substrate, leading to two different reaction trajectories: the bottom- or side-bound pathways. An analogous mechanism was proposed for the regioselectivity of the diynes, as illustrated in Scheme 1b. Because of the steric demands of the supporting ligands, it was envisioned that conventional Grubbs catalysts, such as **Ru1**, may follow a bottom-bound pathway,¹¹ favoring the *E*-isomer in most instances. In contrast, **Ru2** is thought to adopt an unusual side-bound geometry¹² owing to a combination of steric and electronic effects of the chelating NHC ligand, leading to high *Z*-selectivity.¹³ As illustrated in Scheme 1b, the steric demands of the functionalized alkyne substrate and the carbene fragment in **Ru1** and similar Grubbs catalysts of the conventional type may direct the insertion to produce the α -

rather than the β -addition product.^{14–16} For **Ru2**, on the other hand, the α -addition may cause unfavorable steric interactions between the substituent of the side-bound alkyne and the mesityl moiety of the NHC ligand, forcing the β -addition to be preferred.¹⁰ These stereochemical models propose an explanation as to why α - and β -addition are seen with **Ru1** and **Ru2** systems, respectively.

To confirm these previously observed trends and establish a consistent foundation, we carried out a series of experiments using various diyne monomers **M1–M5** (Table 1, entries 1–5). As expected, **Ru1** gives excellent regiocontrol, and we were unable to detect any six-membered ring with ¹³C NMR technique, thereby confirming the exclusive selectivity for α -addition of at least 99:1.^{2a,17} As anticipated based on the previous report,¹⁰ the reversed preference was observed in general with the **Ru2** catalyst favoring the β -addition when reacting with monomer **M1** (entry 6). Unfortunately, only those monomers derived from malonates showed good β -selectivity, and the other monomers (**M2–M5**, entries 7–10) displayed practically no such selectivity. Clearly, the monomer scope and the level of regiocontrol for β -selective cyclopolymerization is not satisfactory. This problem was previously recognized, but the reason for the low selectivity was not known. To better understand these observations, we reexamined the mechanism leading to the regiocontrol by employing a quantum chemical model based on the density-functional theory¹⁸ with the goal of pinpointing the reason for the lack of performance and increasing the regioselectivity toward β -addition.

Table 1. Cyclopolymerization of Various 1,6-Heptadiynes Using Ru1 and Ru2^a

entry	cat	monomer	conv. ^b (%)	yield ^c (%)	M_n^d (kDa)	PDI ^d	5:6 ^e
1	Ru1	M1	>99	69	8.9	1.12	>99:1
2	Ru1	M2	>99	73	15.2	1.34	>99:1
3	Ru1	M3	>99	98	10.1	1.26	>99:1
4	Ru1	M4	>99	97	12.6	1.11	>99:1
5	Ru1	M5	>99	82	12.7	1.12	>99:1
6 ^{fg}	Ru2	M1	88	43	15.6	1.54	1:6.5
7 ^f	Ru2	M2	58	50	7.0	1.53	1:1.5
8 ^f	Ru2	M3	>99	75	10.4	1.97	~1:1
9 ^f	Ru2	M4	96	79	13.1	1.65	1:1.7
10 ^f	Ru2	M5	62	49	6.3	1.41	1:1.4

^aReaction conditions: for the reaction using Ru1, 0.5 M in tetrahydrofuran (THF), 30 min; for the reaction using Ru2, 0.25 M in THF, 3 h. ^bDetermined from ¹H NMR. ^cPrecipitated in MeOH at -78 °C. ^dDetermined from THF-SEC (SEC = size-exclusion chromatography). ^e5-Membered/6-membered rings, determined from ¹³C NMR. ^fPrecipitated in hexane at -78 °C. ^gM/I = 50.

Catalytic Mechanism. Our computer model follows the generally established mechanism for alkyne metathesis,^{13,19} as highlighted in Figure 1. Unsymmetrical alkynes can have two different demands at the first insertion stage. After the formation of reactant complex **1**, the diyne substrate engages in an α -insertion to give ruthenacyclobutene **A-2**. Following ring-opening and insertion of the second alkyne, bicyclic intermediate **A-4** is furnished. The final ring-opening recovers the ruthenium carbene catalyst with the appended carbocycle. In contrast, β -addition at the initial stage gives a six-membered carbocycle by following a similar mechanism as outlined for the α -addition. Although we followed the generally accepted mechanism as previously proposed, our studies suggest a very different reason for the regioselectivity than assumed to date.

Ru1- and Ru2-Catalyzed Cyclopolymerizations. Parts a and b of Figure 2 show the calculated reaction energy profiles of the insertion step mediated by Ru1 and Ru2 catalysts. In the Ru1 system, the cyclopolymerization begins with the catalyst **1-0** that subsequently forms **1A-1**, a π -complex with the heptadiyne substrate at 10.4 kcal/mol. The transition state **1A-1-TS** to afford the α -addition product is found at a relative free energy of 19.0 kcal/mol, which is 9.2 kcal/mol lower than for the transition state **1B-1-TS**, which leads to the β -addition product. This dramatic kinetic preference predicted for the α -addition at the insertion step is in excellent agreement with experimental results, where no β -addition product could be detected. Interestingly, the ruthenacyclobutene intermediate is not a proper minimum on the potential energy surface, as it ring-opens spontaneously to give the carbene intermediates **1A-3** and **1B-3** at -15.7 and -8.1 kcal/mol, respectively.

When Ru2 is used, the reactant π -complex could not be obtained in our computer simulations, as the [2 + 2] cycloaddition was extremely facile and our attempts to locate the π -complex routinely gave the ruthenacyclobutene intermediate instead. We were able to locate the two transition states **2A-1-TS** and **2B-1-TS** at very low barriers of only 7.6 and 3.9 kcal/mol, respectively. This relatively low barrier of 3.9 kcal/mol is fully consistent with the experimental observation that the cyclopolymerization can be conducted at temperatures as low as -40 °C, and this is the temperature at which we conducted the cyclopolymerization to maximize the β -selectivity.¹⁰ The estimated barrier difference of 4 kcal/mol between the α - and β -additions appears overestimated as the observed selectivity is not high. However, because the computations qualitatively agree with the experimental observations, we sought to understand the origin of the predicted selectivity in greater detail. The ruthenacyclobutene intermediates **2A-2** and **2B-2**, which we were not able to optimize in the Ru1 system, were located with the Ru2 system. They were almost isoenergetic with -12.2 and -12.5 kcal/mol barriers, respectively. These ring intermediates can be isomerized to **2A-6** and **2B-6** by interchanging the position of the chelating nitrate ligand and the ruthenacycle moiety. The following ring-opening transition states **2A-6-TS** and **2B-6-TS** lead to exergonic adducts **2A-7** and **2B-7** at -26.6 and -28.7 kcal/mol, respectively. The computer simulations are in excellent agreement with the experimental results that explain the observed selectivity. For both Ru1 and Ru2, the first insertion step is selectivity-determining, because the overall cyclopolymerization process is considered to be irreversible.

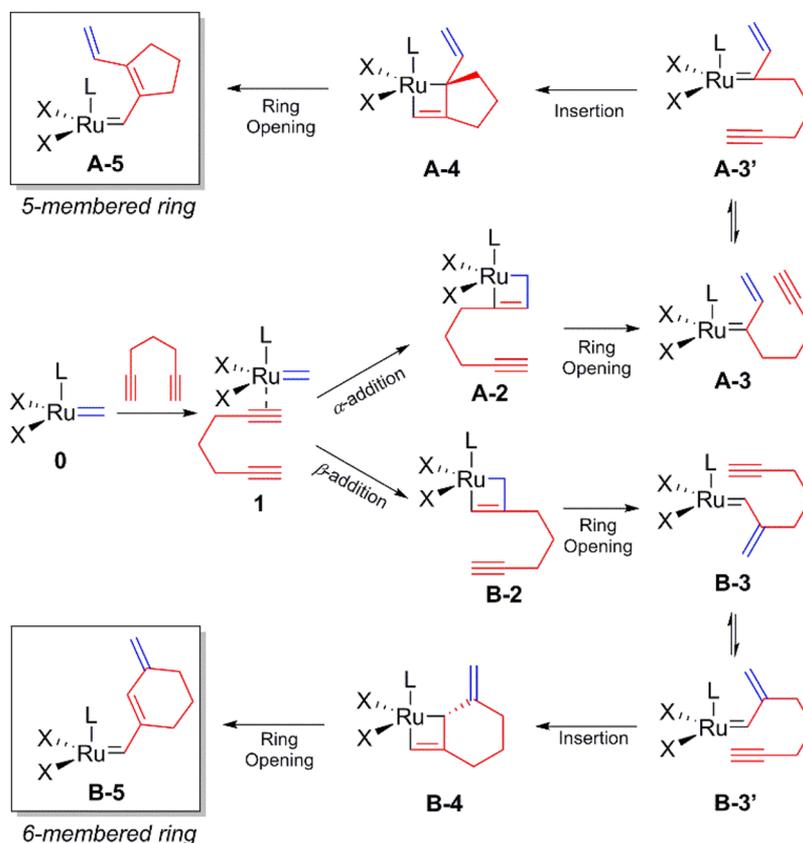


Figure 1. Generalized illustration of the catalytic mechanisms of the Ru-catalyzed alkyne cyclopolymerization.

Origin of the Selectivity. In conclusion, the strategy for inverting the regioselectivity by forcing the alkyne to bind in a side-on fashion is plausible but problematic, because the high reactivity associated with this pathway diminishes the selectivity. After some explorations, we concluded that attempts toward optimizing the **Ru2**-type catalyst to increase the β -selectivity, for example, by functionalizing the NHC ligand, are not promising. Instead, a completely different strategy for regiocontrol based on the electronic demands of the Ru-carbene functionality emerged, as outlined in Figure 3. The Ru-catalysts are Fischer carbenes, and the carbene fragment is best envisaged as a neutral ligand acting as a σ -donor and π -acceptor. Fischer carbenes have two major orbital interactions: (i) σ -donation of sp^2 -orbital of carbene carbon and (ii) π -backdonation from an empty p -orbital of the carbene center. Consequently, the carbene carbon is an electrophile illustrated with a red “+”-sign in Figure 3a.²⁰ Both electronic and steric effects can determine the regioselectivity of cyclopolymerization. Because the less-substituted terminal position is more nucleophilic among the two alkyne carbons of the substrate, the substrate–catalyst alignment leading to the α -addition is electronically preferred. The alignment leading to the β -addition, on the other hand, is electronically mismatched and disfavored. On the contrary, the steric demand of each catalyst shows clearly opposing properties, as illustrated in Scheme 1b. In the octahedral **Ru1** catalyst with bottom-bound demand, the steric hindrance between the metal carbene and the substituents in heptadiyne disfavors the β -addition. The **Ru2** catalyst following side-bound mechanism prefers the β -addition sterically, as the substituents avoid the bulky mesityl group on

the NHC ligand decorating the Ru catalyst as mentioned earlier.

This opposing effect of the electronic and steric factors on cyclopolymerization enables us to understand which of the two properties dominates over each **Ru1** and **Ru2** catalyst. Previously, only steric controls were considered as the origin of the different selectivity in cyclopolymerization; however, we tried to link the electronic effect to switch the regiochemical outcome. The α -addition of **Ru1** catalyst is clearly preferred by both steric and electronic demands, as it exclusively produces the sterically and electronically favored five-membered rings. **Ru2** looks to follow the steric control only as the β -addition is sterically preferred with the side-bound system; however, we cannot exclude the electronic control because the catalyst structure of **Ru2** is very different from that of **Ru1**, which is expected to lead to different carbene electronic properties.

The structure of catalyst **Ru2** is under equilibrium between octahedral and trigonal-bipyramidal scaffolds due to the transient Ru–O bond. As explained in Figure 3c, the $Ru-d_{xy}$ orbital energy level of trigonal-bipyramidal is higher than that of the octahedral geometry. On the other hand, the $Ru-d_{x^2-y^2}$ orbital in trigonal-bipyramidal structure is lower in energy compared to that found in the octahedral geometry. This energy-level difference ultimately changes the electrophilicity of the metal carbene moiety, where the electrophilicity of the carbene carbon may be reduced significantly by increased π -backdonation from the $Ru-d_{xy}$ into the empty carbene- p orbital. Consequently, we believe that the reduced electrophilicity demand of **Ru2** compared to **Ru1** as well as the intrinsic steric preference will be responsible for the inverted regiochemical outcome. We cannot fully establish that the electronic effect

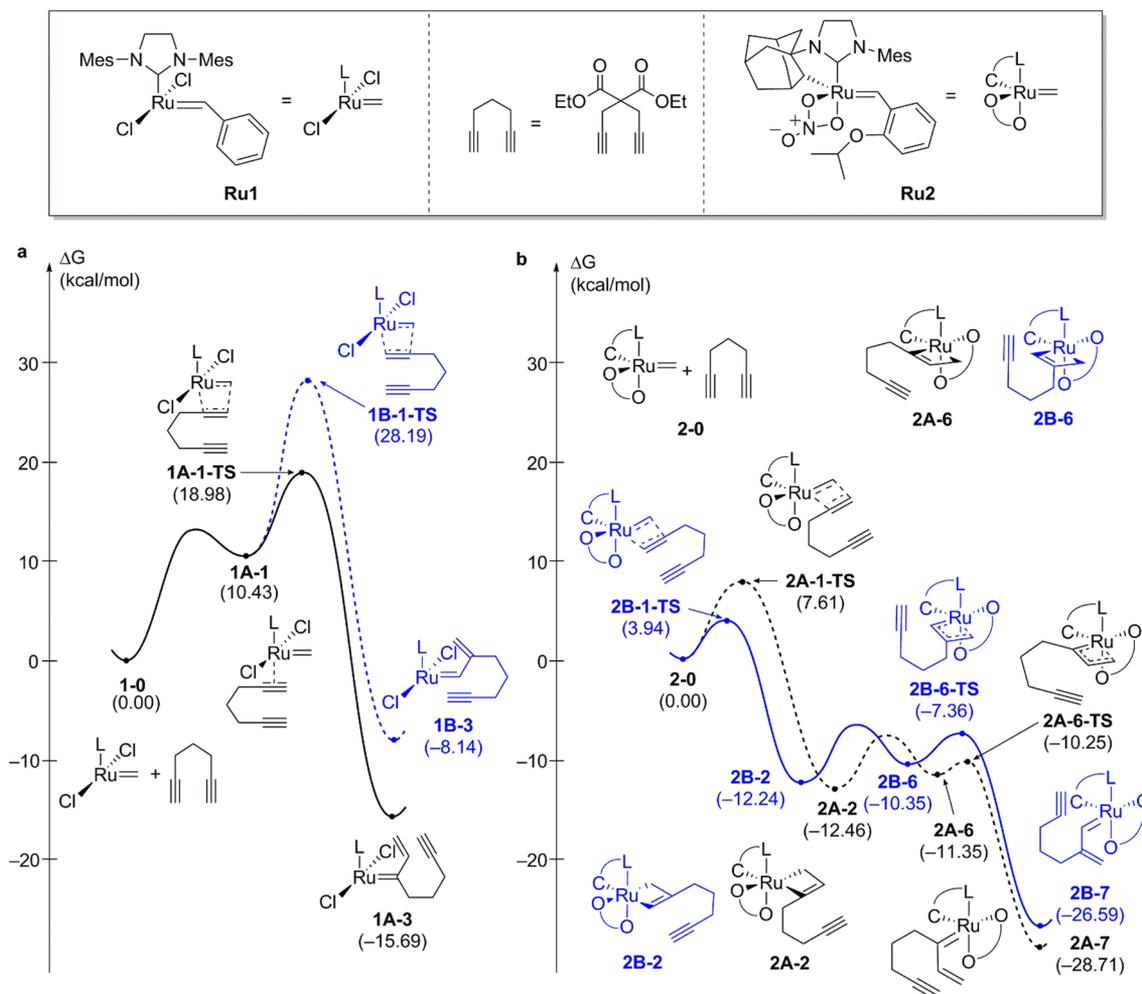


Figure 2. Computed free energy diagrams for the first insertion and ring opening step of the (a) **Ru1** system and the (b) **Ru2** system (black, α -addition; blue, β -addition; solid line, favored; dashed line, disfavored).

dominates the steric effect with **Ru2**, as the catalyst structure is not rigid, but we questioned if the electronic effect can be employed to control the regioselectivity. The electronic effect can be enhanced by enforcing a stringent trigonal-bipyramidal geometry at the metal center, which raises the Ru- d_{xy} energy, as illustrated in Figure 3c.

Complete Switch of the Regioselectivity. These opposing trends in the electronic and steric demands may be an exploitable feature for engineering regioselective cyclopolymerizations. As mentioned above, we expect that the electronic bias toward α -addition is decreased in trigonal-bipyramidal catalysts, as the electrophilicity of the carbene is reduced via π -backdonation. In general, octahedral catalysts should display the intrinsic preference for α -addition that is programmed into the Fischer carbene systems, as explained earlier. This intuitive structure-selectivity relationship was thus far not recognized, and no attempts were made to exploit this feature for gaining regiocontrol over cyclopolymerizations. Accordingly, the regioselectivity was very sensitive to the catalyst structure, as shown in Figure 3d.

The **Ru1** catalyst displays an octahedral coordination geometry, where the carbene is arranged in the same plane as the two chloride ligands due to the orientation of the *N*-heterocyclic carbene ligand. Therefore, π -backdonation is less pronounced; the carbene in the **Ru1** catalyst is electrophilic and

the catalyst is α -selective, representing the typical reactivity profile of a classical Fischer carbene catalyst. The **Ru2** catalyst, however, shows an equilibrium between an octahedral and a trigonal-bipyramidal structure and displays selectivity only at moderate levels. We tested Hoveyda's *Z*-selective catalyst (**Ru3**),^{21,22} a new Ru-based catalyst for cyclopolymerization that has a strict trigonal-bipyramidal structure. **Ru3** adopts a trigonal-bipyramidal coordination geometry and should show β -selective cyclopolymerizations according to our conceptual proposal on the electrophilicity, as long as the standard side-bottom reaction pathway²³ with respect to the NHC ligand is followed. This catalyst contains a bidentate catecholthiolate ligand, where the two anionic ligands were forced to be arranged in a *syn* orientation to each other to give high reactivity and *Z*-selectivity in various cross-metathesis reactions.²⁴ Figure 4 shows the computed free energy diagram of the cyclopolymerization using **Ru3**. The catalysis starts by **Ru3** engaging the diyne reactant to form **3-1** at 7.5 kcal/mol. Interestingly, the β -insertion is associated with a barrier of only 13.5 kcal/mol, which is 7.0 kcal/mol lower than what is found for the α -insertion. The reaction continues by the ruthenacyclobutene intermediate **3B-2** undergoing a structural rearrangement to afford intermediate **3B-6** that ring-opens to give **3B-7**. This reaction energy profile suggests a complete reversal of the regioselectivity seen with **Ru1**, where both the computed

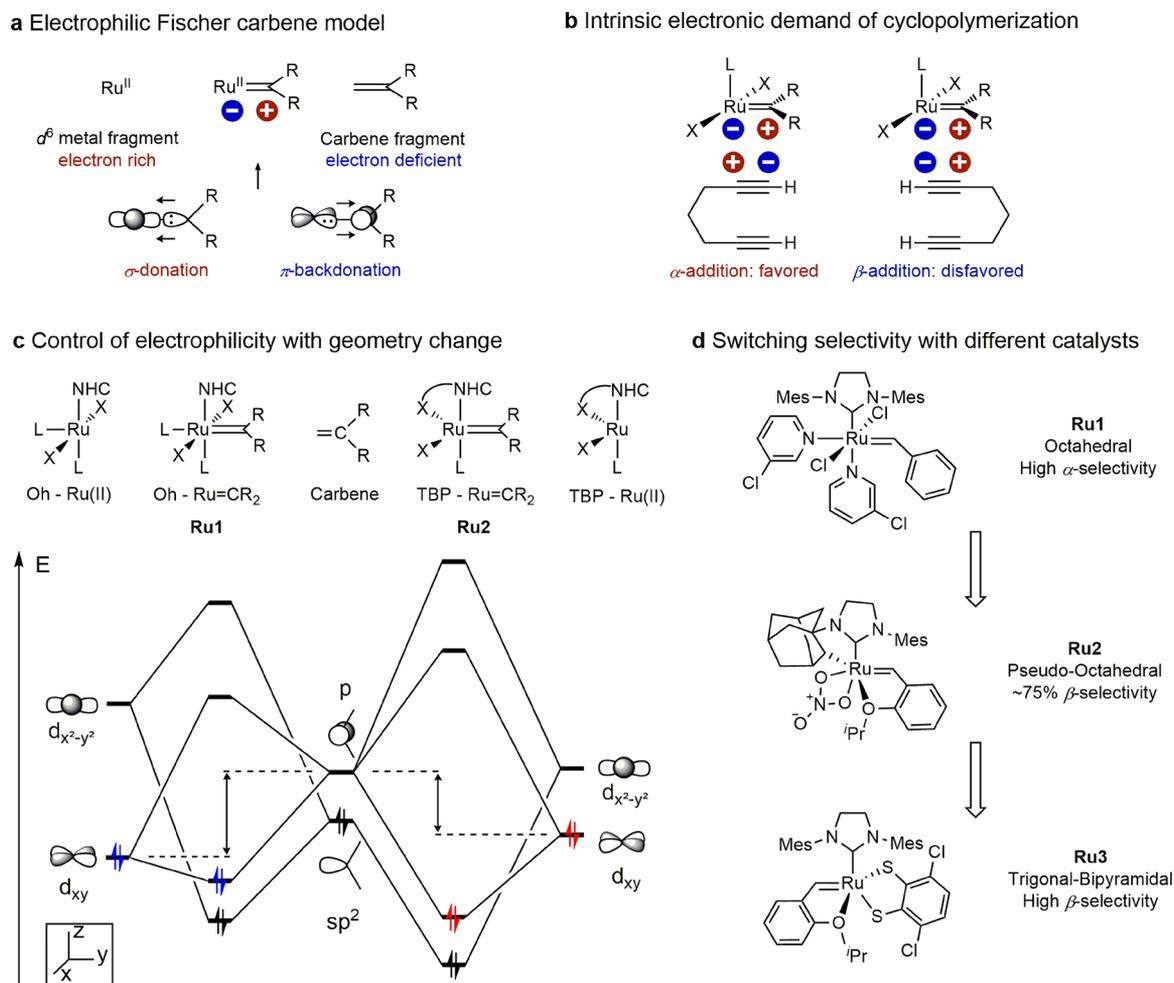


Figure 3. (a) Electrophilic Fischer carbene model and its key metal–ligand interaction. (b) Intrinsic electronic demand of a typical Ru-Fischer carbene with a 1,6-heptadiyne substrate. (c) Qualitative molecular orbital diagram of carbene complexes. (d) Complete switch of regioselectivity by using different Ru(II) catalysts posing different geometries.

barriers of 14–19 kcal/mol for the preferred pathway and the difference to the other regioisomer of ~ 7 kcal/mol are comparable. Thus, we anticipate a similar reactivity profile in terms of catalyst performance and degree of selectivity for **Ru1** and **Ru3**, except for the fact that the selectivities are entirely reversed. If correct, **Ru3** may allow for overcoming the performance problems such as narrow monomer scope and moderate β -selectivity at ambient temperature that were encountered previously with **Ru2**.

In excellent agreement with both the conceptual model and the explicit calculations discussed earlier, we found a dramatic improvement in the selectivity for the β -addition when **Ru3** is used as the polymerization catalyst. Initially, we employed substrate **M1** containing *tert*-butyl malonate in a monomer-to-catalyst (*M/I*) ratio of 30:1 at room temperature (entry 1 of Table 2). To our delight, the resulting conjugated polymer **P1** contained a very high proportion of six-membered rings in the polymer (1:16.6, 94% six-membered ring) even at room temperature. This finding is a significant improvement of the β -selectivity compared to **Ru2**, which showed a lower six-membered ring composition (1:6.5) at room temperature. Higher selectivity of 1:13.8 was only possible by lowering the temperature to -40 °C with prolonged reaction time over 24 h,¹⁰ which is easy to understand with the given computed reaction energy profile discussed earlier. A different *tert*-butyl

ester-containing substrate **M2** also exhibited high β -selectivity using **Ru3**, while **Ru2** resulted in poor selectivity (1:11.8 vs 1:1.5, entry 2). To test for a broader substrate scope, we introduced weaker chelating ether groups (**M3–M5**). As expected from the computed reaction energy profiles discussed earlier, the monosubstituted diyne **M3** also produced the conjugated polyene bearing six-membered ring exclusively when polymerized at room temperature (entry 3). This selectivity is remarkable because the analogous cyclopolymerization using **Ru2** showed no selectivity at all ($<1:99$ vs 1:1, entry 3), but it is entirely consistent with the computed profiles shown in Figure 4. With an increased steric influence in bis-silyl ether monomer **M4**, the cyclopolymerization proceeded more efficiently and retained the excellent β -selectivity, unlike what was seen when **Ru2** was used ($<1:99$ vs 1:1.7, entry 4). Finally, a monomer containing both ester and bulky ether moieties underwent complete conversion and exclusive β -addition at room temperature ($<1:99$ vs 1:1.4, entry 5). The last three results represent the first examples of producing conjugated polyenes with complete six-membered ring repeating units using a user-friendly Ru catalyst system, and they highlight the dramatic improvement of regiocontrol and monomer scope that the new strategy enables.

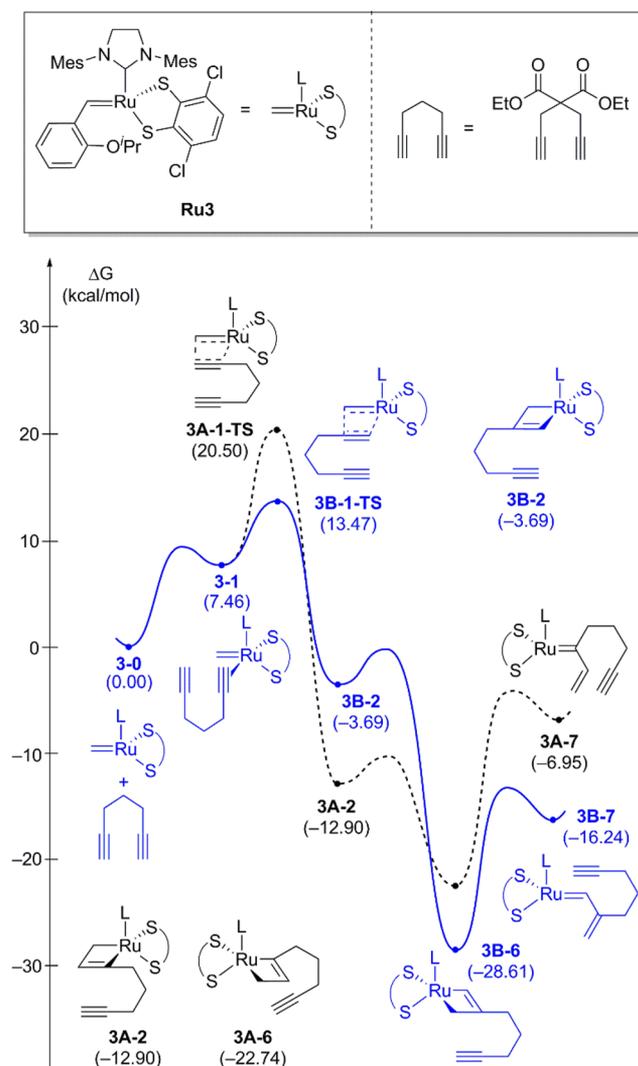
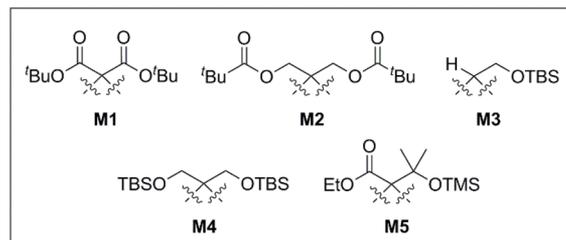
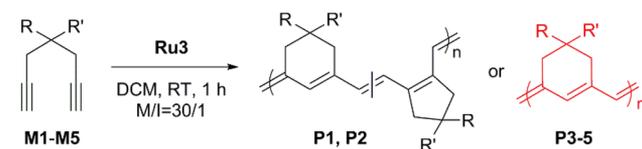


Figure 4. Computed free energy diagram for the first insertion and ring opening step of the **Ru3** system (black, α -addition; blue, β -addition; solid line, favored; dashed line, disfavored).

CONCLUSION

In summary, we found that the classical Grubbs catalyst **Ru1**, which is calculated to favor α - over β -addition by 9.2 kcal/mol, produced conjugated polymers only containing five-membered rings for all substrates (**M1–M5**) via α -addition. Our theoretical analysis showed that this outcome is most consistent with the electronic demands of a classical Fischer carbene catalyst. Two different strategies for engineering regiocontrol and forcing the electronically disfavored β -addition were tested. The first strategy involves changing the substrate binding site. By diverting the reaction from a bottom- to a side-bound channel using the **Ru2** catalyst, a different steric demand is created that overrides the intrinsic electronic preference for α -addition and gives the β -addition product. Our density-functional theory (DFT) calculations show good agreement with the experimental observations that **Ru2** is much more reactive than **Ru1** with an insertion barrier that is lower by >10 kcal/mol. As a result, significant levels of regioselectivity can be seen only at very low temperatures, although the barrier leading to the β -addition is calculated to be significantly lower than that for α -addition. A second new approach to regiocontrol is devised by exploiting the fact that the carbene in trigonal-

Table 2. β -Selective Cyclopolymerization of Various 1,6-Heptydiynes Using **Ru3**



entry	monomer	conv. ^a (%)	yield ^b (%)	M _n ^c (kDa)	PDI ^c	5:6 ^d
1 ^e	M1	95	93	16.1	1.71	1:16.1
2	M2	84	53	15.3	1.61	1:11.8
3	M3	51	47	6.7	1.51	<1:99
4	M4	>99	89	19.6	1.79	<1:99
5	M5	>99	70	25.8	1.92	<1:99

^aDetermined from ¹H NMR. ^bPrecipitated in MeOH at -78 °C. ^cDetermined from THF-SEC. ^d5-Membered/6-membered rings, determined from ¹³C NMR. ^ePrecipitated in hexane at -78 °C.

bipyramidal Ru-catalysts will be much less electrophilic due to stronger π -backdonation. In these complexes, the electronic preference for α -addition is reduced and steric factors may become more important. The *Z*-selective Hoveyda catalyst **Ru3** was calculated and experimentally confirmed to be an ideal system for β -selective cyclopolymerization to exclusively produce six-membered rings in the polymer backbone. Thus, we propose a novel conceptual theory for establishing regiocontrol and show that it is possible to carry out cyclopolymerizations with Ru-catalysts with unprecedented levels of regioselectivity, allowing for the production of a new class of conjugated polymers with potential applications in designing new optoelectronic materials. The strategy of exploiting the electronic properties of the Fischer carbenes is intuitively pleasing and is shown to be powerful. The underlying principles should be generally valid and inspire additional future work on Schrock carbenes that display a completely reversed electronic demand—the carbenes in these systems are best conceptualized as dianionic carbenes and show nucleophilic characteristics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b11968.

Experimental details, characterization data, and Cartesian coordinates of all computed structures and energy components (PDF)

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Notes

The authors declare no competing financial interest.

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