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Article

Ruthenium Olefin Metathesis Catalysts Containing Six-Membered Sulfone and Sulfonamide Chelating Rings

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The preparation and X-ray structure characterization of new olefin metathesis initiators containing sulfone- and sulfonamide-substituted benzylidene ligands are described. We observed that these catalysts exhibit Ru···O(SO)R interactions, forming six-membered chelates. Tuning the electronic and steric factors of the benzylidene part as well as selecting the proper NHC ligands can have a direct impact on catalyst activity and stability, leading to promising new catalysts.

1. Introduction

The metathesis reaction is among the most useful C−C bond-forming transformations, as it can provide valuable intermediates for the synthesis of specialty chemicals and bioactive or natural products.[1,2] It is well-known that ruthenium alkylidene complexes are reasonably tolerant to air and moisture.[3] Although a broad variety of different metathesis initiators have been created, it is still expected that their impact on fine chemical production will increase. Many research groups and industrial companies continue to explore possible improvements in the attainable turnover number, catalyst loading, and metal impurities in the resulting products and are tuning the existing ruthenium complexes to specific requirements of technological processes (Figure 1).[4,5] A great deal of research is directed toward catalysts designed especially to be used at low loadings and in environmentally friendly solvents.[6,7]

Recently, our group introduced the stable sulfur Hoveyda-type derivatives **VII** and **IX**, which demonstrate some fine-tuning abilities.[8,9] Independently, Lemcoff disclosed **VIII**,

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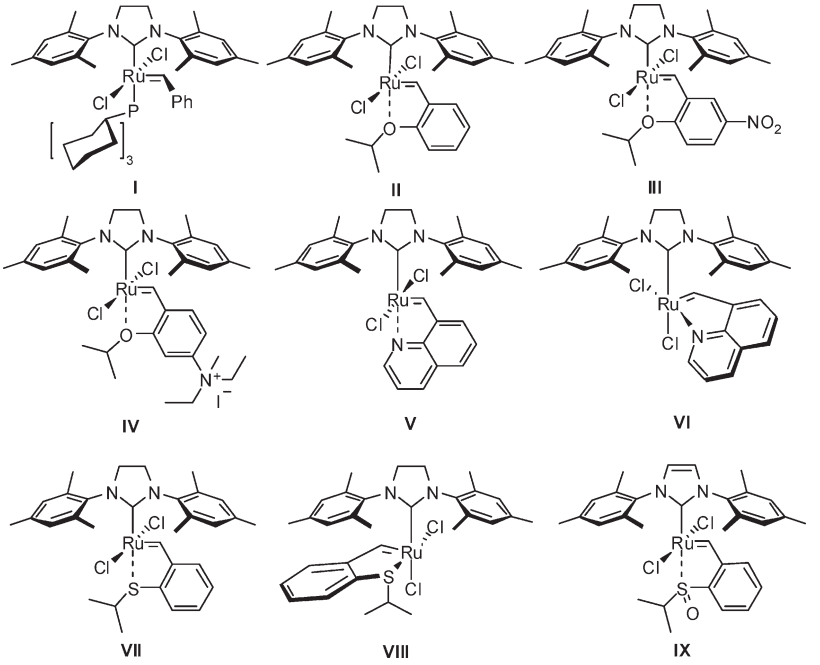


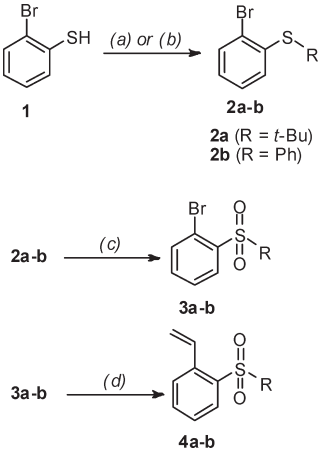
Figure 1. Selected Ru catalysts for olefin metathesis.

showing that the complex is highly tunable and reaching the conclusion that it is the cis isomer of **VII**.[10] Later, in a joint project, the kinetics of **VII** → **VIII** isomerization was studied by us.[11] The promising features of the catalysts shown, such as excellent thermodynamic and air stability combined with good catalytic activity at elevated temperatures, motivated us to direct our research into developing other ligands for ruthenium initiators based on a sulfone chelating motif. We became interested in determining whether an oxidation of the sulfur atom from S^{II} (**VII**) and S^{IV} (**IX**) to the +6 oxidation state would give viable catalyst precursors. While the previously prepared initiators **VII** and **IX** were rather latent in nature because they possess a strong five-membered Ru···S chelating ring, we envisioned that the new complexes stabilized via weaker six-membered Ru···O chelation should exhibit a much higher initiation rate. Additionally, we decided to explore the NHC ligand influence on the stability of these complexes.

2. Results and Discussion

Synthesis and Characterization of New Complexes. During previous research on **IX**, we realized that the steric bulk of the substituent at sulfur directly influences the catalyst activity. The same observation was made earlier by Lemcoff during his detailed study on differently substituted cis isomers of complex **VIII**.[10] Our starting point was to check the respective steric and electronic influences of the R substituents at the sulfur atom on the stability and activity of the relevant initiators. For the preparation of the required ligand precursors, we used synthetic pathways similar to those exploited in the case of sulfoxide complexes **IX** in our previous contributions. The commercially available 2-bromothiophenol (**1**) was transformed into sulfone-bearing ligand precursors **4a**,**b** by oxidation of sulfides **2a**,**b** with

Scheme 1. Synthetic Pathway to Sulfone Ligands Containing *tert*-Butyl and Phenyl Groups[a]



[a] Reagents and isolated yields: (a) *t*-BuOH, H_2SO_4/H_2O, −10 °C → room temperature, 24 h (58%). (b) C_6H_5I, CuI, sodium *tert*-butoxide, neocuproine, toluene, reflux, 24 h, (65%); (c) Oxone, MeOH, 5 °C → room temperature, 4 h (**3a**, 75%; **3b**, 76%);[14] (d) $Pd(PPh_3)_2Cl_2$, $CH_2{=}CHBF_3K$, Cs_2CO_3, THF/H_2O, 85 °C, 22 h (**4a**, 80%; **4b**, 82%).

2 equiv of Oxone[12] and Suzuki−Miyaura cross-coupling with potassium (vinyl)trifluoroborate as the key steps (Scheme 1).[13]

Having the ligands in hand, we made attempts to form complexes, first containing *t*-Bu substituents to cause steric hindrance. At the same time, we were prompted to evaluate the possible influence of the nature of the NHC on the behavior of these complexes. In the first attempt to form complexes containing a *t*-Bu substituent, **Xa**−**XIIa**, we chose a standard ligand exchange reaction, which required using different terms presented in Scheme 2. In the case of initiators **Xa** and **XIa**, syntheses were performed in the presence of

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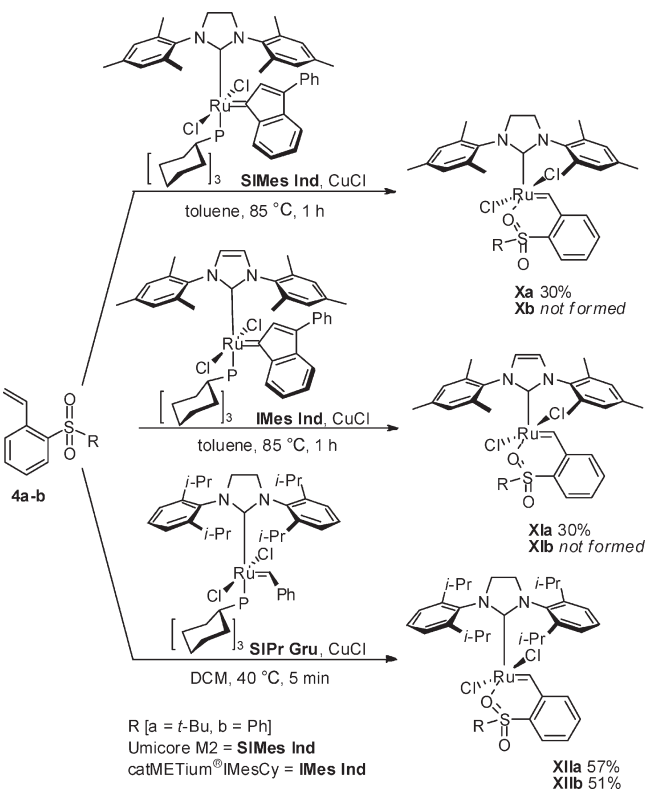
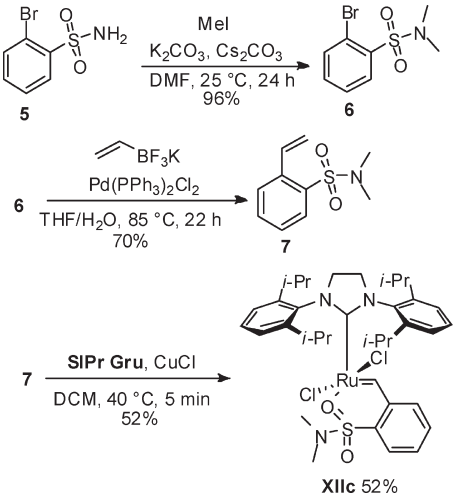
Scheme 2. New Ru Initiators with Sulfone Ligands Containing *tert*-Butyl and Phenyl Groups



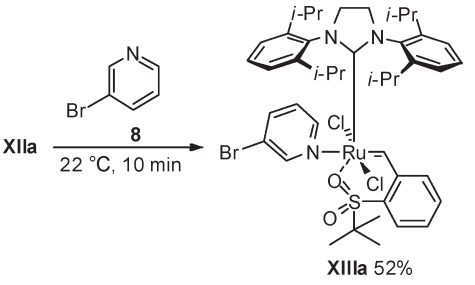
CuCl, in toluene at 85 °C with indenylidene catalysts,[15] while the procedure developed for **XIIa** was based on the application of more favorable and milder conditions (40 °C and dichloromethane). As a ruthenium source we used **SIPr Gru**—a derivative of Grubbs' second-generation catalyst. The SIPr NHC ligand is known to form very stable Ru complexes.[16] The corresponding products **Xa** and **XIa** were isolated in rather poor yields (~30%); however, to our satisfaction, catalyst **XIIa** was formed in 57% yield as light green microcrystals. The new ruthenium compound **XIIa** was found to be stable in air as well in solution, which allowed us to fully characterize it by spectral techniques and elemental analysis.

Encouraged by these first successes, we decided to continue the preparation of analogous complexes bearing a phenyl substituent at the sulfone group (**Xb** and **XIb**); however, this turned out to be more problematic. During the reaction between **4b** and the appropriate indenylidene ligands SIMes-Ind and IMes-Ind, we observed the initial formation of green spots on the TLC plates which disappeared completely before **SIMes Ind** and **IMes Ind** were consumed. Although syntheses of **Xb** and **XIb** ended up unsuccessfully, in the case of **XIIb** we obtained the corresponding sulfone catalyst in 51% yield, using the SIPr

Scheme 3. Synthetic Pathway of a Sulfonamide bearing Precursor 7 and Catalyst XIIc



Scheme 4. Synthesis of Catalyst XIIIa



Grubbs complex (**SIPr Gru**). We surmised that the stability of SIPr-containing complexes **XIIa**,**b** is due to a combination of steric hindrance at the benzylidene moiety with increased steric bulk for the NHC ligand, which leads to more stable initiators.

Next, we considered synthesizing a complex containing a sulfonamide functionality at the benzylidene ligand. To prepare ligand **7**, we used a different protocol. The synthesis began from the commercially available 2-bromobenzenesulfonamide **5**, which was converted by alkylation[17] and Suzuki−Miyaura cross-coupling into compound **7** (Scheme 3).[13]

Taking into consideration the observed lower stability of SIMes and IMes complexes, we decided to limit our synthesis to a catalyst containing the SIPr ligand. We performed the exchange reaction using the SIPr Grubbs catalyst (**SIPr Gru**), which led to **XIIc** as dark green microcrystals in 52% yield (Scheme 3).

Next, we synthesized a modification of the original architecture of catalyst **XIIa**, which led to the synthesis of initiator **XIIIa** containing 3-bromopyridine as an additional labile ligand.[18] The complex **XIIIa** was prepared by adding an excess of 3-bromopyridine (**8**) to **XIIa**. The reaction was complete within 10 min, without the need to use any solvent or column chromatography as a purification step. The best way to obtain the analytically pure initiator **XIIIa** was to

(14) For other synthetic methods to obtain **3b**, see: Truce, W. E.; Amos, M. F. *J. Am. Chem. Soc.* **1951**, *73*, 3013–3017.

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(17) To compare the analytical data of **6**, see: Pines, S. H.; Purick, R. M.; Reamer, R. A.; Gal, G. *J. Org. Chem.* **1978**, *43*, 1337–1342.

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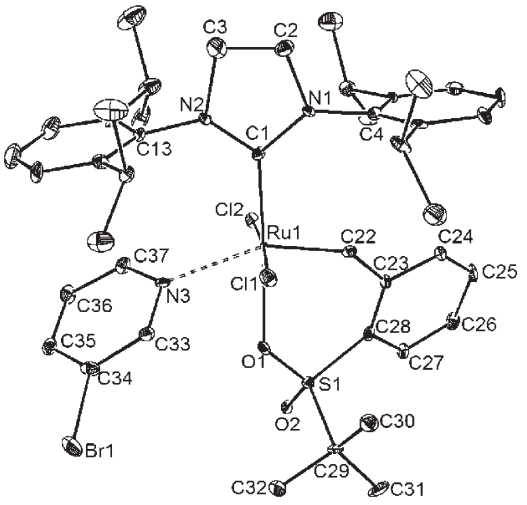


Figure 2. ADPs (atom displacement parameters) and labeling of atoms in **XIIIa**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

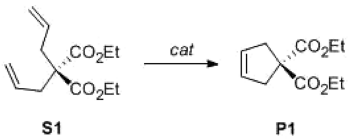
precipitate it slowly from a mixture of dichloromethane and *n*-heptane. The final light green microcrystalline solid was isolated in 52% yield (Scheme 4).

Crystals suitable for X-ray diffraction studies were obtained from a crystallization process at a temperature of +4 °C using the same system of solvents as for the precipitation step with the addition of diethyl ether. This manipulation allowed us to confirm the structure of **XIIIa** (Figure 2).

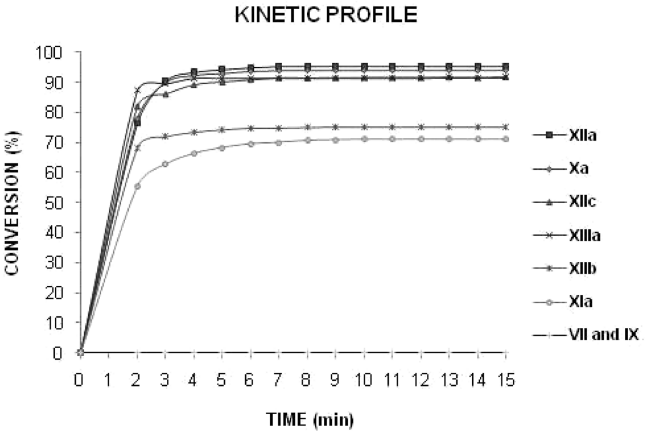
A single crystal of the compound XIIIa (Figure 2) grows from a 1/1/1 DCM/diethyl ether/*n*-heptane mixture in the triclinic $P\bar{1}$ space group. There is one molecule of the catalyst and two molecules of solvent in the independent part of the unit cell. The molecules of solvents are diethyl ether and a half-molecule of the *n*-heptane moiety (C200−C204 with the C204 atom in the close neighborhood of the symmetry center). The most important structural parameters for this structure are given in Table 1. In comparison to earlier presented structures containing the sulfur atom,[8a] the geometry of this molecule is quite unique, due to significant changes in the ruthenium coordination sphere. Because for the first time the benzylidene ring is substituted by a sulfone group, the ruthenium atom is coordinated by one of the oxygen atoms (O1). This creates a six-membered Ru1−C22−C23−C28−S1−O1 ring with a Ru1−C22−C23−C28 torsion angle value equal to −32.7(15)°, instead of an almost planar five-membered ring, as in the Hoveyda catalyst Ru1−C22−C23−C28−O1[3e] and Ru1−C22−C23−C28−S1[8] in the sulfur **VII** and sulfoxide **IX** derivatives of the Hoveyda catalyst. Other significant geometry changes include Ru(1)−C(1) bond shortening and elongation of Ru−Cl bonds (see Table 1), which can be justified also by the presence of a 3-bromopyridyne ligand.

Moreover, in the solid state the catalyst participates in stacking interactions at distances of 3.224−3.297 Å, thus forming some special catalyst−substituent−substituent−catalyst associations (Figure 3). The interaction is enabled by two 3-bromopyridine rings reversed and bound to different molecules of catalyst. These "dimers" of the catalyst molecules form planes in three dimensions, where the NHC ligand domains (including the solvent molecules) are threaded with the benzylidene−ruthenium−3-bromopyridine domains.

Scheme 5. RCM of S1[a]

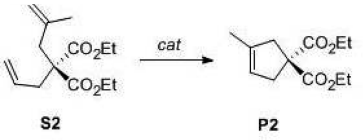


S1 P1

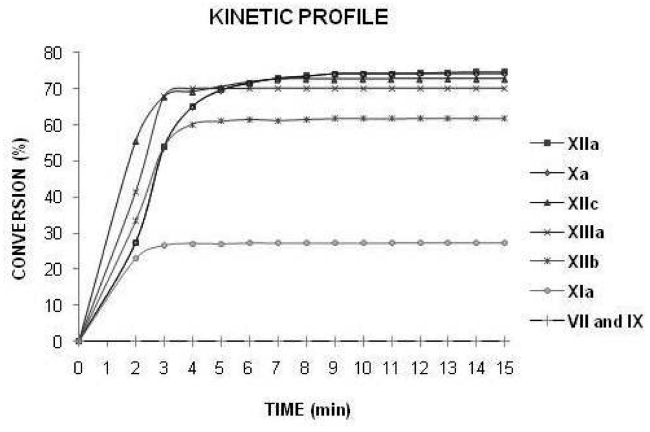


[a] Conditions: *c*[**S1**] = 0.1 M, 1 mol % of catalyst, CD_2Cl_2, 22 °C, 15 min.

Scheme 6. RCM of S2[a]



S2 P2



[a] Conditions: *c*[**S2**] = 0.1 M, 1 mol % of catalyst, CD_2Cl_2, 22 °C, 15 min.

Comparison of Catalyst in Tested Reactions. In order to evaluate the catalytic performance of all initiators, a set of model RCM reactions was carried out to picture structure −activity relationships in the given class of the catalysts. Activity profiles of complexes bearing the same benzylidene ligand were used to establish a thorough evaluation of the "NHC nature" effect. The model substrates selected by us included various substituted and functionalized dienes and enynes, and all reactions were run with 1 mol % of initiator. At first, the reactivity profiles of these novel SO_2-chelating complexes were measured by ^{1}H NMR spectroscopy using common substrates: diethyl diallylmalonate (**S1**; Scheme 5) and diethyl allyl(2-methylallyl)malonate (**S2**; Scheme 6).

Table 1. Comparison of Geometrical Parameters for Crystal Forms of Selected Structures[a]

geometrical params	SIMes_S_iPr (**VII**)	IMes_SO_iPr (**IX**)	SiPr_SO2_tBu_Py (**XIIIa**)
		Bond Lengths (Å)	
Ru(1)−C(1)	2.054(1)	2.080(6)	1.985(9)
Ru(1)−C(22)	1.830(2)	1.841(7)	1.852(10)
Ru(1)−X(1)	2.440(1)	2.366(2)	2.245(7)
Ru(1)−Cl(1)	2.339(1)	2.334(4)	2.420(3)
Ru(1)−Cl(2)	2.338(1)	2.316(2)	2.361(3)
Ru(1)−N(3)			2.303(8)
C(22)−C(23)	1.460(2)	1.457(9)	1.463(13)
C(23)−C(28)	1.402(2)	1.385(9)	1.414(13)
S(1)−C(28)	1.778(2)	1.775(7)	1.756(10)
S(1)−C(29)	1.856(2)	1.806(8)	1.818(10)
S(1)−O(1)			1.457(7)
S(1)−O(2)		1.486(5)	1.442(6)
		Planar Angles (deg)	
Ru(1)−C(1)−N(1)	131.8(1)	133.5(5)	127.9(7)
Ru(1)−C(1)−N(2)	120.6(1)	123.4(4)	126.4(7)
Cl(1)−Ru(1)−Cl(2)	156.75(1)	156.54(7)	176.18(10)
Ru(1)−C(22)−C(23)	122.8(1)	124.6(5)	126.3(7)
C(1)−Ru(1)−X(1)	175.2(4)	175.4(2)	177.0(3)
C(22)−C(23)−C(28)	119.1(1)	118.4(6)	126.9(9)
N(3)−Ru(1)−C(22)			156.9(4)
		Torsion Angles (deg)	
C(28)−S(1)−O(1)−Ru(1)			1.9(7)
C(22)−Ru(1)−O(1)−S(1)			−29.1(6)
C(22)−Ru(1)−S(1)−C(28)	−16.4(1)	−8.4(3)	
Ru(1)−C(22)−C(23)−C(28)	2.054(1)	−7.5(8)	−32.7(15)
C(13)−N(2)−C(1)−Ru(1)	1.830(2)	14.3(9)	−7.2(16)
C(4)−N(1)−C(1)−Ru(1)	2.440(1)	−15.4(10)	20.6(16)

[a] X(1) is the atom coordinated to the ruthenium center (S(1) for **VII** and **IX** and O(1) for **XIIIa**).

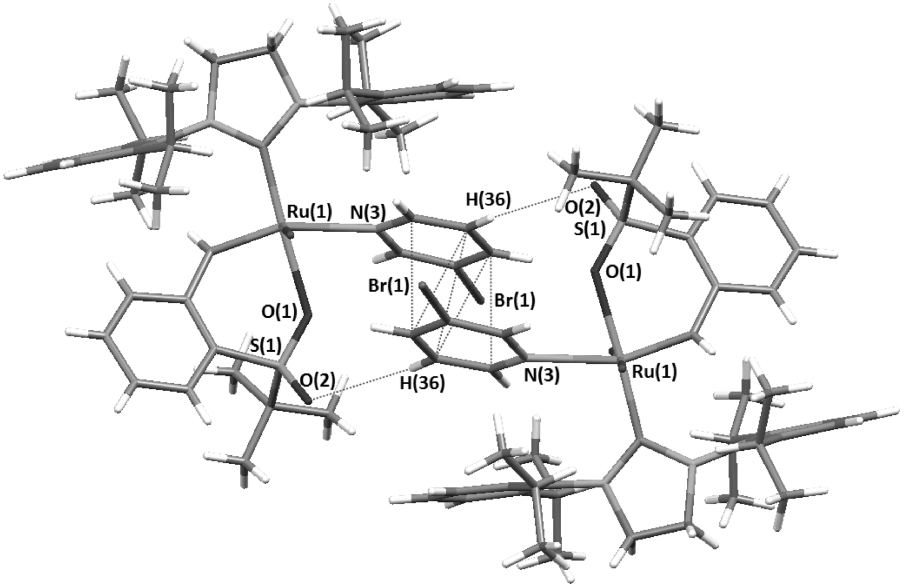
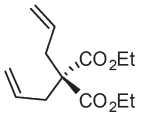
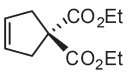
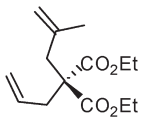
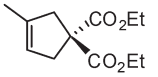
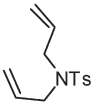
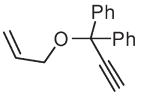
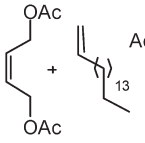
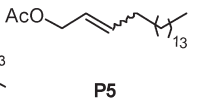


Figure 3. Dimer formed by two molecules of catalyst **XIIIa** and two molecules of 3-bromopyridine.

As expected, sulfone complexes **XIIa**, **Xa**, **XIIIa**, and **XIIc**, bearing the saturated NHC SIPr and SIMes ligands, were found to be more active than the **XIa** derivative containing the unsaturated NHC (respectively 95% and 71%). Unfortunately catalyst decomposition prevents achieving full conversion, thus leaving unconverted **S1**. In the case of **XIIb** (initiator with phenyl substituent), we assumed that despite the presence of a more bulky ligand in the structure of the catalyst, electronic factors caused instability of the complex and, as a consequence, lower conversion during the catalytic performance (75%). However, it is worth noting that all initiators operate at room temperature in the RCM reaction of **S1**, providing a very high yield of **P1** in less than 10 min (Scheme 5). For a better comparison, we imposed additional reactivity data for the sulfur and sulfoxide congeners **VII** and **IX** on the same graph. Previously, we indicated that these ruthenium compounds showed a remarkable thermal stability in different solvents, but it makes them useful only at

Table 2. Additional RCM and CM for New Initiators[a]

entry	substrate	product	catalyst/loading (mol%)	time (min)	temperature (°C)	conversion/ yield (%)
1	 **S1**	 **P1**	**XIIa** (1)	15	0	72
			Xa (1)	15	0	70
			XIIc (1)	15	0	70
			XIIb (1)	15	0	60
			XIa (1)	15	0	26
			XIIIa (1)	15	0	69
2	 **S2**	 **P2**	**XIIa** (1)	15	0	54
			Xa (1)	15	0	51
			XIIc (1)	15	0	49
			XIIb (1)	15	0	43
			XIa (1)	15	0	9
			XIIIa (1)	15	0	52
3	 **S3**	 **P3**	**XIIa** (1)	15	22	97
			Xa (1)	15	22	97
			XIIc (1)	15	22	95
			XIIb (1)	15	22	95
			XIa (1)	15	22	80
			XIIIa (1)	15	22	97
4	 **S4**	 **P4**	**XIIa** (1)	15	22	95
			Xa (1)	15	22	94
			XIIc (1)	15	22	94
			XIIb (1)	15	22	93
			XIa (1)	15	22	77
			XIIIa (1)	15	22	94
5	 **S5a** **S5b**	 **P5** *E*/*Z* = 10:1	**XIIa** (2)	30	22	73
			Xa (2)	30	22	69
			XIIc (2)	30	22	64
			XIIb (2)	30	22	55
			XIa (2)	30	22	36
			XIIIa (2)	30	22	70

[a] Conditions: (RCM) $c = 0.1$ M, CH_2Cl_2; (CM) $c = 0.2$ M, CH_2Cl_2, 2 equiv of substrate **S5a**. Conversions were determined by GC for entries 1−5. In case of entry 5, the yield after chromatographic purification is given (E/Z = 10/1).

higher temperature (from 80 to 110 °C).[8] At the same time, sulfone congeners are characterized by faster initiation rates which are associated with a lower stability, especially in solution, allowing for a successful execution of metathesis reactions at lower temperatures (from 0 to 22 °C).

To examine the application profile of our catalysts in more detail, we conducted the RCM reaction with diethyl allyl(2-methylallyl)malonate (**S2**), which is a more demanding substrate than **S1**. The conversion plots in Scheme 6 showed similar tendencies in the relative performance of complexes.

We observed little difference in reactivity trends using **XIIa**, **Xa**, and **XIIc** (from 72 to 74%). These results may be explained by a stabilizing effect due to the steric hindrance of the *tert*-butyl group and the presence of a strong electron-donating group in the benzylidene moiety.[19] On the other hand, complex **XIIb**, with a phenyl substituent, and **XIa**, containing an IMes ligand, turned out to be much less active under such conditions (respectively 61% and 27%).

Comparing the influence of an additional ligand on the catalytic behavior of initiator **XIIIa** required following the same metathesis reactions and correlating the results with those obtained for other complexes. This allowed us to monitor the difference in the initiation rates, stabilities and the overall performance of catalysts. Kinetic studies confirmed examples available in the literature.[20] The third-generation complex **XIIIa** proved to be a very fast initiator, giving 87% yield for **S1** and 41% for **S2** just after 2 min (in Schemes 5 and 6, respectively) with a noticeably lower overall activity (91% (**S1**) and 70% (**S2**)) than in the case of **XIIa**.

Other representative examples of RCM and CM reactions are shown in Table 2. Although the first two transformations presented (entries 1 and 2) were conducted at 0 °C with low catalyst loading (1 mol %), they proceeded in good yield within 15 min. Cyclizations of unhindered diene **S3** and enyne **S4** were achieved in almost quantitative yields in less than 0.5 h. The last example of efficiency of sulfone-based catalysts, shown in entry 5, demonstrates the utility in the CM reaction even at room temperature. It is worth mentioning that in this case **P5** is the only product, as the conditions applied in the reaction prevent self-metathesis of **S5b**. To obtain a complete picture of the activity of catalyst **XIIIa**, we repeated the procedure applied for other analogues. The results received for **XIIIa** follow previously observed reactivity trends toward model substrates shown in Table 2 for **XIIa**. It is also worth noting that the analogue **XIIIa** presented higher stability in different solvents in comparison to congeners **XIIb** and **XIa**.

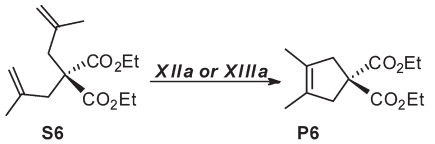
In light of these results, we investigated the catalytic activity toward tetrasubstituted diene **S6** using the most promising initiators: **XIIa** and **XIIIa**. (Table 3).

We found that complex **XIIa** applied at low loading (1 mol %) at 40 °C in CH_2Cl_2 resulted in only 2% conversion of substrate **S6** after 15 min. Even when the reaction time was

(19) Grela, K.; Kim, M. *Eur. J. Org. Chem.* **2003**, 963–966.

(20) (a) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035–4037. (b) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314–5318.

Table 3. RCM of S6 using XIIa and XIIIa



S6 P6

entry	solvent	temperature (°C)	loading (mol%)	yield (%) XIIa	yield (%) XIIIa
1	CH_2Cl_2	40	1	2	0
2	CH_2Cl_2	40	5	14	5
3	toluene	80	5	21	9

[a] Conditions: *c*[**S6**] = 0.1 M, 15 min, 1 and 24 h.

prolonged to 1 and 24 h, no change in the conversion was noted, as used catalysts tend to decompose at elevated temperatures. Increasing the initiator's loading to 5 mol % and heating the reaction mixture to 40 and 80 °C was not helpful, as we obtained only slightly improved conversions, from 14% to 21% for **XIIa** and 5% to 9% for **XIIIa**. These findings forced us to conclude that although the new catalysts (**XIIa** and **XIIIa**) present increased reaction rates at low temperatures as compared to the second-generation Hoveyda catalyst (**II**), they fail to conduct a ring closure that gives tetrasubstituted olefins. It should be noted that the latter transformation is problematic also for **Gru-II** and **Hov-II** catalysts.[1g] Probably the approach of an increasingly bulky substrate causes difficulties in metathesis and promotes decomposition of active species, due to steric hindrance in the NHC ligand and weaker stabilization of the sulfone group.

3. Conclusions

In summary, we have reported the syntheses and characterization of new sulfone and sulfonamide chelating active Ru initiators. The investigation of their catalytic activity, especially in the RCM reactions at low temperatures, pointed out their good applicability to unhindered and moderately hindered substrates. The analysis of the structure−catalytic performance relationship proved that these new initiators can be tuned by changing the steric and electronic environments of the benzylidene and NHC ligand. It is worth highlighting that the SO_2 group increases the reactivity of the ruthenium complexes, which combined with the good stability provided by SIPr ligands leads to the promising stable and active catalysts **XIIa** and **XIIIa**.[21] The formal oxidation of sulfur atom from +2 to +6 gives rise to new "rocket" catalysts, which are expected to find applications in metathesis science. Related ongoing research on sulfur-containing catalysts will be reported in due course.

4. Experimental Section[22]

4.1. Synthesis of Ligand Precursors. Compounds **2a**,**b** were synthesized according to literature procedures.[8a]

4.1.1. Oxidation Reaction (3a and 3b). Water (4 mL) and Oxone (2.60 g, 4.1 mmol) were placed in a three-necked, round-bottomed flask, equipped with a stirrer, thermometer, and an addition funnel with a pressure-equalization arm. The mixture was cooled to 5 °C and vigorously stirred, while a solution of the appropriate sulfide (2.1 mmol) in MeOH (4 mL) was placed in the funnel and added dropwise to the stirred slurry. After addition of the sulfide the reaction mixture was stirred at room temperature for 2 h. Subsequently, methanol was removed on a rotary evaporator. The remaining solution was extracted with methylene chloride (2 × 5 mL). The combined organic layers were dried over $MgSO_4$, concentrated to ca. 3 mL, filtered through a plug of silica gel, and washed with an additional 3 mL of CH_2Cl_2. The colorless filtrate was concentrated, and the resulting oil or solid was dried under vacuum at room temperature to provide a corresponding sulfone (yield of 75−76%).

1-Bromo-2-(*tert*-butylsulfonyl)benzene (3a). Colorless crystals, yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 9H), 7.39−7.54 (m, 2H), 7.73−7.84 (m, 1H), 8.02−8.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 62.5, 122.9, 127.5, 134.4, 134.9, 135.1, 136.4. MS (EI; *m*/*z* (relative intensity)): 39 (19), 41 (12), 56 (26), 57 (100), 58 (30), 75 (29), 76 (27), 77 (24), 156 (29) 158 (29), 278 (67). IR (KBr): ν 3087, 3064, 2985, 2970, 2934, 2868, 2004, 1978, 1951, 1864, 1779, 1748, 1665, 1573, 1563, 1476, 1447, 1424, 1390, 1370, 1363, 1300, 1275, 1262, 1214, 1196, 1170, 1137, 1124, 1095, 1037, 1024, 977, 940, 893, 798, 777, 771, 739, 709, 656, 630, 571, 520, 480 cm^{-1}. Anal. Calcd for $C_{10}H_{13}SBrO_2$: C, 43.33; H, 4.72; S, 11.57; Br, 28.83. Found: C, 43.52; H, 4.87; S, 11.46; Br, 28.94. Mp: 90−91 °C.

1-Bromo-2-(phenylsulfonyl)benzene (3b). Yellowish crystals, yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.47 (m, 1H), 7.48−7.56 (m, 3H), 7.57−7.63 (m, 1H), 7.64−7.73 (m, 1H), 7.89−8.02 (m, 2H), 8.35−8.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.2, 127.9, 128.6, 128.48, 131.4, 133.4, 134.6, 135.6, 139.8; MS (EI; *m*/*z* (relative intensity)): 50 (10), 51 (16), 75 (12), 76 (11), 125 (56), 153 (9), 203 (54), 205 (64), 296 (45), 298 (44). HRMS (EI; *m*/*z*): calcd for $[M]^{+\bullet}$ ($C_{12}H_9S^{79}BrO_2$) 295.950 66, found 295.950 66. IR (KBr): ν 3079, 3067, 1955, 1884, 1845, 1648, 1570, 1474, 1447, 1427, 1316, 1282, 1249, 1176, 1154, 1132, 1104, 1081, 1066, 1027, 999, 882, 839, 771, 756, 741, 711, 681, 648, 614, 584, 565, 502, 489, 449, 415 cm^{-1}. Anal. Calcd for $C_{12}H_9SBrO_2$: C, 48.50; H, 3.05; S, 10.79; Br, 26.89. Found: C, 48.41; H, 3.24; S, 10.53; Br, 26.63. Mp: 116−118 °C.

4.1.2. Alkylation Reaction (2-Bromo-*N*,*N*-dimethylbenzenesulfonamide (6)). To a suspension of K_2CO_3 (1.05 g, 8 mmol) and Cs_2CO_3 (0.312 g, 0.96 mmol) in DMF (10 mL) was added 2-bromobenzenesulfonamide **5** (0.76 g, 3.2 mmol). After the mixture was stirred for 30 min, iodomethane (1 g, 0.44 mL, 7.04 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. Then the mixture was poured into water (8 mL) and extracted with diethyl ether (2 × 10 mL); the combined organic phases were washed with water and brine and dried over $MgSO_4$. Solvent was removed in vacuo, and the crude product was purified by column chromatography, using as an eluent pure cyclohexane and later a cyclohexane/ethyl acetate mixture (10/1 v/v) to give **6** as colorless crystals (0.48 g, yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.76−3.03 (s, 6H), 7.28−7.59 (m, 2H), 7.65−7.85 (m, 1H), 7.99−8.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.3, 120.4, 127.5, 132.3, 133.5, 135.7, 137.8. MS (EI; *m*/*z*) (relative intensity)): 42 (23), 44 (100), 155 (50), 157 (55), 184 (13), 219 (14), 221 (18), 263 (42). IR (KBr): ν 3087, 3028, 2915, 1848, 1806, 1496, 1994, 1958, 1925, 1874, 1836, 1732, 1646, 1574, 1565, 1473, 1448, 1424, 1344, 1268, 1257, 1171, 1159, 1127, 1100, 1053, 1039, 1023, 957, 767, 748, 701, 688, 644, 578, 535, 512, 480, 440 cm^{-1}. Anal. Calcd for $C_8H_{10}SBrNO_2$: C, 36.38; H, 3.82; S, 12.14; Br, 30.25; N, 12.14. Found: C, 36.31; H, 3.77; S, 12.14; Br, 30.05; N, 5.31. Mp: 55−57 °C.

4.1.3. Suzuki-Miyaura Cross-Coupling (4a,b and 7). A solution of potassium (vinyl)trifluoroborate (0.32 g, 2.36 mmol), $PdCl_2(PPh_3)_2$ (0.044 g, 0.065 mmol), Cs_2CO_3 (2.1 g, 6.45 mmol),

(21) For other S-containing catalysts, see: (a) Monfette, S.; Fogg, D. E. *Organometallics* **2006**, *25*, 1940–1944. (b) Katayama, H.; Nagao, M.; Ozawa, F. *Organometallics* **2003**, *22*, 586–593. (c) Bieniek, M.; Bujok, R.; Stępkowska, H.; Jacobi, A.; Hagenkötter, R.; Arlt, D.; Jarzembska, K.; Woźniak, K.; Grela, K. *J. Organomet. Chem.* **2006**, *691*, 5289–5297.

(22) For full experimental details and other information see the Supporting Information.

and a suitable sulfone (2.15 mmol) in THF/H_2O (9/1 v/v) (10 mL) was heated at 85 °C under an argon atmosphere in a Schlenk tube. The reaction mixture was stirred at this temperature for 22 h and then cooled to room temperature and diluted with H_2O (6 mL) followed by extraction with DCM (3 × 10 mL). The combined organic phases were dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by silica gel column chromatography (using cyclohexane/ethyl acetate 10/1 to 1/1 v/v) to obtain the corresponding styrene (70−82% yield).

1-(*tert*-Butylsulfonyl)-2-vinylbenzene (4a). Colorless crystals, yield 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11−1.52 (s, 9H), 5.39−5.45 (dd, J = 1.1, 11 Hz, 1H), 5.66−5.73 (dd, J = 1.0, 17 Hz, 1H), 7.40−7.46 (m, 1H), 7.57−7.63 (m, 1H), 7.67−7.72 (m, 1H) 7.81−7.88 (m, 1H) 7.93−7.96 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.8, 61.5, 118.2, 127.5, 128.1, 132.4, 133.1, 133.7, 134.9, 140.2. MS (EI; m/z (relative intensity)): 41 (17), 57 (100), 58 (5), 77 (10), 103 (7), 104 (12), 119 (8), 137 (20), 168 (45) 224 (7). IR (KBr): ν 3058, 3032, 2975, 2934, 2869, 2003, 1947, 1864, 1676, 1622, 1590, 1560, 1467, 1411, 1397, 1364, 1318, 1281, 1270, 1203, 1171, 1132, 1114, 1047, 1020, 1010, 1000, 897, 800, 776, 760, 738, 699, 649, 633, 590, 571, 556, 521, 475 cm^{-1}. Anal. Calcd for $C_{12}H_{16}SO_2$: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.06; H, 7.23; S, 14.06. C. Mp: 109−111 °C.

1-(Phenylsulfonyl)-2-vinylbenzene (4b). Yellowish crystals, yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.30−5.32 (dd, J = 1.2, 11 Hz, 1H), 5.50−5.52 (dd, J = 1.1, 17 Hz, 1H), 7.43−7.49 (m, 5H), 7.49−7.52 (m, 1H), 7.83−7.88 (m, 3H), 8.18−8.21 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 118.9, 127.6, 127.7, 128.0, 128.3, 128.9, 129.3, 133.0, 133.2, 133.7, 137.7, 138.0, 141.6. MS (EI; m/z (relative intensity)): 51 (20), 77 (43), 91 (100), 153 (11), 165 (24), 178 (23), 179 (42), 180 (12), 197 (9), 213 (8), 244 (10). IR (KBr): ν 3090, 3067, 3028, 1905, 1845, 1776, 1692, 1654, 1622, 1582, 1560, 1477, 1464, 1448, 1407, 1317, 1309, 1296, 1283, 1196, 1152, 1124, 1090, 1070, 1043, 1021, 999, 919, 883, 850, 795, 776, 760, 721, 689, 595, 575, 561, 520, 482, 434 cm^{-1}. Anal. Calcd for $C_{14}H_{12}SO_2$: C, 68.83; H, 4.95; S, 13.12. Found: C, 68.66; H, 4.88; S, 12.97. Mp: 76−78 °C.

***N*,*N*-Dimethyl-2-vinylbenzenesulfonamide (7).** Yellow oil, yield 70%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.74−2.77 (s, 6H), 5.41−5.43 (dd, J = 1.2, 11 Hz, 1H), 5.66−5.70 (dd, J = 1.2, 17 Hz, 1H), 7.38−7.42 (m, 1H), 7.53−7.57 (m, 2H), 7.63−7.61 (m, 1H), 7.93−7.78 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 37.4, 118.1, 127.6, 128.4, 130.1, 132.9, 134.5, 134.7, 137.9. MS (EI; m/z (relative intensity)): 42 (17), 44 (34), 51 (20), 77 (67), 78 (14), 91 (12), 102 (25), 103 (86), 104 (54), 119 (10), 132 (78), 146 (100), 211 (67). IR (KBr): ν 3554, 3091, 3065, 3027, 2962, 2928, 2884, 2850, 2813, 1849, 1732, 1625, 1591, 1563, 1468, 1412, 1342, 1284, 1270, 1200, 1159, 1123, 1051, 1022, 996, 955, 931, 883, 795, 772, 756, 718, 674, 595, 567, 537, 479, 458, 425 cm^{-1}. Anal. Calcd for $C_{10}H_{13}SNO_2$: C, 56.85; H, 6.20; S, 15.18; N, 6.63. Found: C, 56.65; H, 6.34; S, 15.29; N, 6.42.

4.2. General Syntheses of Catalysts. 4.2.1. Synthesis of Catalyst Xa. A Schlenk tube equipped with a stirring bar was charged with a ruthenium complex (**Ind SIMes**; 0.34 g, 0.5 mmol) and CuCl (0.055 g, 0.55 mmol). The tube was flushed with argon and charged with anhydrous toluene (15 mL). Styrene **4a** (0.135 g, 0.6 mmol) in anhydrous toluene (10 mL) was added, and the resulting mixture was stirred at 85 °C for 1 h. After this time, TLC indicated a complete conversion of the substrate. The resulting mixture was concentrated in vacuo, the residue was dissolved in AcOEt, and the solution was passed through a Pasteur pipet containing a small amount of cotton and evaporated to dryness. The crude product was purified by column chromatography (using cyclohexane/ethyl acetate 10/1 to 1/1 v/v). After evaporation of solvents, the resulting solid was collected and washed a few times with AcOEt and with cold *n*-pentane (0.105 g, 0.15 mmol, yield 30%).

Xa: green microcrystalline solid, yield 30%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.03 (s, 6H), 1.23 (s, 3H), 2.21−2.57 (m, 18H), 4.75−4.25 (m, 4H), 6.91−6.95 (m, 1H), 7.00−7.21 (m, 3H), 7.42−7.53 (m, 1H), 7.61−7.72 (m, 2H), 7.83−7.88 (m, 1H), 18.91 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 17.9, 19.0, 20.3, 21.2, 23.0, 62.9, 64.5, 120.2, 126.4, 129.4, 130.1, 130.6, 132.3, 135.8, 137.7, 138.3, 138.7, 139.5, 141.4, 147.3, 153.8, 209.0, 271.1. MS (FD/FI; m/z): calcd for $[M]^+$ 688.7380, found 688.7357. IR (KBr): ν 3469, 3055, 2953, 2918, 1856, 2734, 1944, 1735, 1607, 1578, 1557, 1481, 1419, 1398, 1381, 1267, 1188, 1133, 1114, 1098, 1062, 1035, 917, 884, 852, 795, 777, 755, 713, 691, 633, 579, 519, 489, 467, 424 cm^{-1}. Anal. Calcd for $C_{32}H_{40}Cl_2O_2N_2RuS$: C, 55.81; H, 5.85; N, 4.07; S, 4.66; Cl, 10.30. Found: C, 55.62; H, 5.79; N, 4.21; S, 4.93; Cl, 10.58.

4.2.2. Synthesis of Catalyst XIa. A Schlenk tube equipped with a stirring bar was charged with a ruthenium catalyst (**Ind IMes**; 0.34 g, 0.5 mmol) and CuCl (0.06 g, 0.6 mmol). The tube was flushed with argon and charged with anhydrous toluene (15 mL). The corresponding styrene **4a** (0.55 mmol) in anhydrous toluene (10 mL) was added. The resulting solution was stirred at 85 °C for 1 h. After this, all manipulations could be done without the protective atmosphere of argon. The resulting mixture was concentrated in vacuo, the residue was dissolved in AcOEt, and the solution was passed through a Pasteur pipet containing a small amount of cotton and evaporated to dryness. The crude product was purified by column chromatography (using cyclohexane/ethyl acetate 10/1 to 1/1 v/v). After evaporation of solvents, the resulting green microcrystalline solid was collected and washed a few times with AcOEt and cold *n*-pentane (0.1 g, 0.146 mmol, yield 30%).

XIa: green microcrystalline solid, yield 30%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.85−1.36 (m, 9H), 2.03−2.46 (m, 18H), 4.06−4.09 (m, 2H), 6.95−7.02 (m, 3H), 7.05−7.15 (m, 2H), 7.45−7.50 (m, 1H), 7.61−7.71 (m, 1H), 7.80−7.88 (m, 1H), 19.04 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.6, 17.7, 18.9, 22.6, 23.3, 23.5, 33.8, 63.1, 64.9, 120.2, 122.3, 124.2, 125.1, 127.2, 128.8, 129.5, 133.1, 133.4, 134.1, 134.7; 136.0, 137.5, 138.0, 139.1, 153.5, 171.7, 298.4. MS (FD/FI; m/z): calcd for $[M]^+$ 686.7122, found 686.7104. IR (KBr): ν 3444, 3161, 3136, 2917, 2856, 2735, 1936, 1734, 1691, 1608, 1578, 1557, 1484, 1463, 1398, 1341, 1315, 1280, 1235, 1191, 1164, 1132, 1098, 1077, 1062, 1036, 973, 962, 923, 884, 862, 795, 778, 743, 713, 692, 633, 589, 572, 519, 487, 429 cm^{-1}. Anal. Calcd for $C_{32}H_{38}Cl_2O_2N_2RuS$: C, 55.97; H, 5.58; N, 4.08; S, 4.67; Cl, 10.33. Found: C, 56.12; H, 5.73; N, 4.21; S, 4.84; Cl, 10.58.

4.2.3. General Synthesis of Catalysts XIIa−c. A Schlenk tube equipped with a stirring bar was charged with a ruthenium complex (**SIPr Gru**; 0.14 g, 0.15 mmol) and CuCl (0.016 g, 0.165 mmol). The tube was flushed with argon and charged with anhydrous CH_2Cl_2 (4.5 mL). The appropriate styrene (0.18 mmol) in anhydrous CH_2Cl_2 (3 mL) was added, and the resulting mixture was stirred at 40 °C for 5 min. After this time, TLC indicated a complete conversion of the substrate. The resulting mixture was concentrated in vacuo, the residue was dissolved in AcOEt, and the solution was passed through a Pasteur pipet containing a small amount of cotton and evaporated to dryness. The crude product was purified by column chromatography (using cyclohexane/ethyl acetate 20/1 to 1/1 v/v). After evaporation of solvents, the resulting green microcrystalline solid was collected and washed a few times with AcOEt and with cold *n*-heptane (51−57% yield).

XIIa: light green microcrystalline solid, yield 57%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.00 (s, 9H), 1.31−1.50 (m, 14H), 1.56−1.63 (m, 2H), 3.68−4.20 (m, 4H), 7.30−7.39 (m, 2H), 7.40−7.45 (m, 2H), 7.50−7.72 (m, 4H), 7.68−8.00 (m, 2H), 18.66 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.9, 21.5, 23.2, 23.6, 23.7, 23.8, 24.1, 24.7, 25.2, 26.7, 27.4, 28.5, 29.9, 34.9, 61.7, 118.2, 122.4, 124.1, 124.5, 125.0, 127.2, 127.5, 128.1, 128.7, 129.9, 130.4, 132.3, 133.1, 133.3, 133.5, 133.7, 134.9, 138.1, 140.2, 148.7, 152.7, 210.7, 295.9. MS (FD/FI; m/z): calcd for $[M]^+$ 772.8943, found 772.8930. IR (KBr): ν 3514, 3062, 2966, 2927, 2867, 1944, 1701, 1629, 1586, 1558, 1464, 1445, 1408, 1396, 1364, 1344, 1325, 1282, 1263, 1233, 1192, 1134, 1100, 1079, 1058, 1023, 994, 933, 884, 804, 758, 738, 726, 713, 691, 633, 590, 580,

567, 551, 519, 489, 457 cm^{-1}. Anal. Calcd for $C_{38}H_{52}Cl_2O_2N_2RuS$: C, 59.05; H, 6.78; N, 3.62; S, 4.15; Cl, 9.17. Found: C, 59.22; H, 6.71; N, 3.56; S, 4.03; Cl, 9.28.

XIIb: dark green microcrystalline solid, yield 51%. ^1H NMR (600 MHz, $CDCl_3$): δ 1.18−1.50 (m, 22H), 2.26 (s, 2H), 3.66−3.78 (m, 3H), 4.08−4.16 (m, 3H), 7.28−7.39 (m, 4H), 7.40−7.50 (m, 2H), 7.52−7.58 (m, 2H), 7.60−7.70 (m, 1H), 7.75−7.95 (m, 4H), 8.15−8.30 (m, 1H), 18.81 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.6, 21.3, 24.3, 25.7, 26.5, 28.7, 60.4, 119.0, 124.8, 127.0, 127.6, 128.0, 128.3, 128.4, 128.5, 128.8, 128.9, 129.2, 129.4, 129.7, 131.9, 133.0, 133.2, 133.3, 133.5, 133.9, 136.6, 137.8, 140.0, 141.9, 148.6, 170.6, 210.3, 298.0. MS (FD/FI; m/z): calcd for $[M]^+$ 792.3456, found 792.3440. IR (KBr): ν 3436, 3062, 2025, 2964, 2926, 2867, 1945, 1697, 1631, 1585, 1557, 1465, 1446, 1408, 1386, 1364, 1323, 1295, 1264, 1234, 1179, 1147, 1120, 1089, 1059, 1024, 998, 931, 885, 852, 804, 776, 758, 723, 688, 633, 597, 571, 459 cm^{-1}. Anal. Calcd for $C_{40}H_{48}Cl_2O_2N_2RuS$: C, 60.59; H, 6.10; N, 3.53; S, 4.04; Cl, 8.94. Found: C, 60.48; H, 5.97; N, 3.58; S, 4.27; Cl, 8.75.

XIIc: green microcrystalline solid, yield 52%. ^1H NMR (600 MHz, $CDCl_3$): δ 0.84−0.89 (m, 2H), 1.05−1.50 (m, 21H), 2.43 (s, 6H), 2.72−2.78 (m, 1H), 3.50−3.80 (m, 2H), 4.11 (s, 3H), 7.30−7.40 (m, 6H), 7.47−7.55 (m, 2H), 7.60−7.65 (m, 3H), 18.64 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.1, 22.6, 23.7, 24.0, 26.2, 26.5, 28.8, 31.6, 37.6, 124.3, 124.7, 127.9, 128.2, 129.6, 130.0, 132.8, 133.5, 148.8, 149.2, 152.3, 152.4, 210.7, 295.7. MS (FD/FI; m/z): calcd for $[M]^+$ 759.8521, found 759.8537. IR (KBr): ν 3501, 3063, 2964, 2927, 2867, 1948, 1731, 1695, 1629, 1586, 1464, 1444, 1409, 1387, 1363, 1326, 1297, 1264, 1234, 1179, 1150, 1114, 1057, 1049, 994, 955, 934, 884, 804, 758, 724, 701, 674, 645, 621, 600, 582, 570, 551, 535, 477, 458 cm^{-1}. Anal. Calcd for $C_{36}H_{49}Cl_2O_2N_2RuS$: C, 56.91; H, 6.50; N, 5.53; S, 4.22; Cl, 9.33. Found: C, 56.72; H, 6.73; N, 5.58; S, 4.08; Cl, 9.61.

4.2.4. Synthesis of Catalyst XIIIa. A Schlenk tube equipped with a stirring bar was charged with a ruthenium complex (**XIIa**; 0.124 g, 0.16 mmol) and 3-bromopyridine (0.390 mL, 0.632 g, 4 mmol). The resulting mixture was stirred at 22 °C for 10 min. After this time, TLC indicated complete conversion of **XIIIa**. The resulting mixture was concentrated in vacuo. The green residue was dissolved in a minimum amount of dichloromethane and washed with cold *n*-heptane (5 mL). The light green precipitate was filtered, washed with *n*-heptane (2×5 mL). and dried under vacuum to afford light green microcrystalline solid **XIIIa** (0.078 g, 0.084 mmol, 52% yield).

XIIIa: light green microcrystalline solid, yield 52%. ^1H NMR (600 MHz, $CDCl_3$): δ 1.01 (s, 9H), 1.15−1.30 (m, 18H), 1.32−1.34 (m, 2H), 1.36−1.38 (m, 2H), 7.15−7.25 (m, 2H), 7.28−7.40 (m, 5H), 7.41−7.45 (m, 2H), 7.57−7.63 (m, 2H), 7.78−7.85 (m, 3H), 18.70 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.4, 23.2, 23.7, 25.8, 26.2, 28.4, 28.8, 63.1, 122.1, 124.6, 127.1, 129.2, 133.1, 134.8, 138.6, 148.3, 149.2, 151.3, 152.6, 210.7, 296.3. MS (FD/FI; m/z): calcd for $[M]^+$ 930.6458, found 930.6460. IR (KBr): ν 3436, 3062, 2959, 2925, 2865, 1935, 1739, 1667, 1628, 1588, 1556, 1463, 1440, 1413, 1390, 1362, 1349, 1325, 1302, 1282, 1264, 1247, 1230, 1194, 1170, 1157, 1134, 1099, 1059, 1045, 1028, 1006, 998, 981, 962, 929, 905, 884, 869, 827, 803, 794, 759, 712, 698, 634, 579, 572, 555, 517, 497, 460, 417 cm^{-1}. Anal. Calcd for $C_{43}H_{56}Cl_2O_2N_3RuBrS$: C, 55.48; H, 6.06; N, 4.51; S, 3.44; Cl, 7.62. Found: C, 55.32; H, 6.19; N, 4.71; S, 3.31; Cl, 7.78.

4.3. General Procedure for Preparative RCM and CM Reactions using Xa, XIa, XIIa−c, and XIIIa. 4.3.1. Time−Conversion Studies. All catalytic reactions were prepared under an inert atmosphere of argon gas. All reactions were run in NMR tubes at 22 °C at a 0.1 M substrate/concentration, and the progress of the reaction was followed by ^1H NMR spectroscopy. Substrates: **S1** and **S2** (0.08 mmol, 19.2 and 20.3 mg, respectively) were dissolved in CD_2Cl_2 (0.7 mL) and then transferred with a syringe to the respective NMR tube. To obtain the required catalyst amount, a solution of suitable ruthenium initiator (0.01 mol, 6 mg) was dissolved in 1 mLof CD_2Cl_2 and 100 μL of this solution was added to a NMR tube. The tube was stirred for a few seconds (the reaction time started at this point) and introduced to the spectrometer (locked and shimmed), and conversions were measured by ^1H NMR.

4.3.2. Time−Conversion Studies. GC Conversions. At 0 °C. Cyclization of substrates: **S1** and **S2** were used as a test to compare the activity of catalysts in CH_2Cl_2 at 0 °C. Typically, 1 mol % of the catalyst (0.008 mmol) was added to a solution of substrate (0.8 mmol) and an internal standard in 8 mL of CH_2Cl_2 at 0 °C. The reaction was run at 0 °C under argon, and samples were taken after 5, 10, and 15 min and analyzed by TLC and GC.

At 22 °C (RCM and Enyne Cycloisomerization). Cyclization of substrates: **S3** and **S4** were used as a test to compare the activity of catalysts in CH_2Cl_2 at 22 °C. Typically, 1 mol % of the catalyst (0.008 mmol) was added to a solution of substrate (0.8 mmol) and an internal standard in 8 mL of CH_2Cl_2 at 22 °C. The reaction was run at 22 °C under argon, and samples were taken after 5, 10, and 15 min and analyzed by TLC and GC.

At 22 °C (CM). Cross-metathesis of **S5a** and **S5b** was used as a test to compare the activity of catalysts in CH_2Cl_2 at 22 °C. Catalyst (2 mol %, 0.012 mmol) was added to a solution of substrates (0.6 mmol for **S5b** and 1.2 mmol for **S5a**) in 3 mL of CH_2Cl_2 at 22 °C. The reaction was run at 22 °C under argon, and samples were taken after 30 min and analyzed by TLC and ^1H NMR.

At 40 °C. Cyclization of diethyl allyl(2-methylallyl)malonate (**S6**) was used as a test to compare the activity of catalysts in CH_2Cl_2 at 40 °C. Catalyst (1 mol %, 0.008 mmol) was added to a solution of substrate (0.8 mmol) and an internal standard in 8 mL of CH_2Cl_2 at 40 °C. The reaction was run at 40 °C under argon, and samples were taken after 15 min and 1 and 24 h and analyzed by GC.

At 40 °C. Cyclization of diethyl allyl(2-methylallyl)malonate (**S6**) was used as a test to compare the activity of catalysts in CH_2Cl_2 at 40 °C. Catalyst (5 mol %, 0.02 mmol) was added to a solution of substrate (0.4 mmol) and an internal standard in 4 mL of CH_2Cl_2 at 40 °C. The reaction was run at 40 °C under argon, and samples were taken after 15 min and 1 and 24 h and analyzed by GC.

At 80 °C. Cyclization of diethyl allyl(2-methylallyl)malonate (**S6**) was used as a test to compare the activity of catalysts in toluene at 80 °C. Catalyst (5 mol %, 0.02 mmol) was added to a solution of substrate (0.4 mmol) and an internal standard in 4 mL of toluene at 80 °C. The reaction was run at 80 °C under argon, and samples were taken after 15 min and 1 and 24 h and analyzed by GC.

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Supporting Information Available: Figures, tables, text, and CIF files giving ^1H NMR and ^{13}C NMR spectra of all new compounds and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.