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Allenylidene-to-Indenylidene Rearrangement in Arene−Ruthenium Complexes: A Key Step to Highly Active Catalysts for Olefin Metathesis Reactions

Ricardo Castarlenas,* Chloé Vovard, Cédric Fischmeister, and Pierre H. Dixneuf*

Contribution from the Institut de Chimie de Rennes, UMR 6509 CNRS−Université de Rennes, Organométalliques et Catalyse, Campus de Beaulieu, 35042 Rennes, France

Received November 23, 2005; E-mail: pierre.dixneuf@univ-rennes1.fr

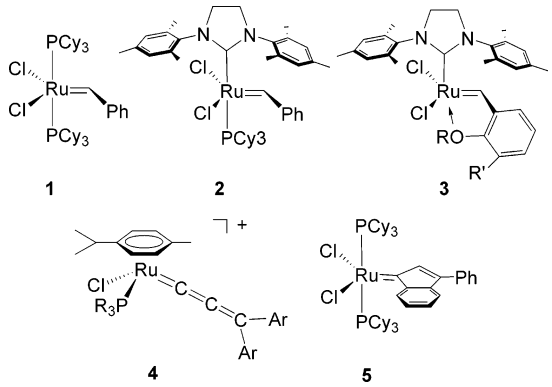
Abstract: The allenylidene−ruthenium complexes [(η^6-arene)RuCl(=C=C=CR_2)(PR'_3)]OTf (R_2 = Ph; fluorene, Ph, Me; PR'_3 = PCy_3, P^iPr_3, PPh_3) (OTf = CF_3SO_3) on protonation with HOTf at −40 °C are completely transformed into alkenylcarbyne complexes [(η^6-*p*-cymene)RuCl(≡CCH=CR_2)(PR_3)](OTf)$_2$. At −20 °C the latter undergo intramolecular rearrangement of the allenylidene ligand, with release of HOTf, into the indenylidene group in derivatives [(η^6-arene)RuCl(indenylidene)(PR_3)]OTf. The in situ-prepared indenylidene−ruthenium complexes are efficient catalyst precursors for ring-opening metathesis polymerization of cyclooctene and cyclopentene, reaching turnover frequencies of nearly 300 s^{-1} at room temperature. Isolation of these derivatives improves catalytic activity for the ring-closing metathesis of a variety of dienes and enynes. A mechanism based on the initial release of arene ligand and the in situ generation of the active catalytic species RuCl(OTf)(=CH_2)(PR_3) is proposed.

Introduction

The discovery of well-defined metal−alkylidene complexes as powerful catalysts for the cleavage and formation of C=C bonds has enabled olefin metathesis to reach impressive developments that have largely improved synthetic methods and contributed to materials science.[1] This many-faceted revolution brought about by alkene metathesis catalysis has just been recognized by the award of the 2005 Nobel Prize in Chemistry to Yves Chauvin for the discovery of mechanisms based on an alkylidene−metal intermediate[2] and to Richard R. Schrock and Robert H. Grubbs for their discovery and fruitful applications of efficient, well-defined molybdenum−alkylidene[1d−f] and ruthenium−alkylidene[1g−i] alkene metathesis catalysts.

Stable alkylidene−ruthenium-based precatalysts have broadened the scope of the reaction due to their high tolerance toward a variety of functional groups while maintaining an excellent catalytic activity. The commercially available complexes $RuCl_2$-(=CHPh)(PCy_3)$_2$ (**1**)[3] and $RuCl_2$(=CHPh)(PCy_3)(NHC) (NHC = N-heterocyclic carbene) (**2**)[4] (Chart 1), in which one hindered phosphine PCy_3 has been replaced by a more electron-donating NHC ligand, have played a key role, showing excellent activity in a large number of applications including ring-opening metathesis polymerization (ROMP),[5] ring-closing metathesis (RCM),[6] acyclic diene metathesis polymerization (ADMET),[7] and cross metathesis (CM).[8] It was established that the release of one phosphine in complexes **1** and **2** to generate a 14-electron intermediate is the determining step of the catalytic reaction.[9]

Chart 1



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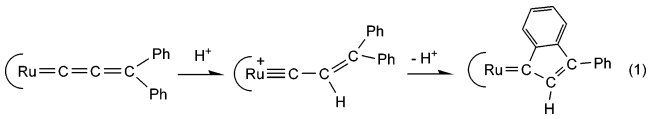
Thus, the introduction of chelating isopropoxybenzylidene ligand[10a] has led to a new type of very active phosphine-free ruthenium−alkylidene catalysts (**3**) that can be easily recovered after achievement of catalytic reaction.[10] More recently, various ruthenium-based metathesis catalysts have been prepared by replacement of one or two chloride ligands.[11]

Despite the profit brought by these neutral ruthenium−alkylidene derivatives, efforts still need to be made to prepare readily accessible, active, and robust catalyst precursors in order to improve the scope of applications and innovate in catalyst or initiator designing. In this context, ruthenium−vinylidene[12] or ruthenium−allenylidene[13−16] derivatives, readily obtained from easy-to-prepare or commercially available ruthenium complexes and simple terminal alkynes or propargyl alcohols, have been revealed as a valid alternative.

The ionic 18-electron ruthenium−allenylidene complexes of formula [(η^6-*p*-cymene)RuCl(=C=C=CAr_2)(PR_3)]X (**4**), generated from [RuCl(PR_3)(*p*-cymene)]X and HC≡CC(OH)Ar_2, promoted RCM of dienes and enynes[13,15,16] as well as ROMP[16] and provided an unprecedented example of the involvement of allenylidenes in alkene metathesis. The catalytic mechanism involves the initial decoordination of the η^6-bound *p*-cymene ligand.[13,17,18] Kinetic and spectroscopic studies have revealed that on thermal activation the ionic 18-electron allenylidene complex **4** actually was progressively transformed into a noncharacterized alkene metathesis catalytic species.[19]

Other ruthenium−allenylidenes, such as $RuCl_2(PCy_3)_2$(=C=C=CPh_2)[14f] and [RuCl(NHC)(arene)=C=C=CAr_2]X,[14g] have led to moderate alkene metathesis catalytic activity. By contrast, an attempt to make $RuCl_2(PPh_3)_2$=C=C=CPh_2 failed, but the formation of an inert $RuCl_2(PPh_3)_2$(ind) (ind = 3-phenylindenylidene) complex was observed instead.[20] The displacement of PPh_3 by PCy_3 actually afforded the active catalyst precursor $RuCl_2(PCy_3)_2$(ind) (**5**) that has displayed excellent performance for a wide range of organic substrates[21] and is now commercially available.

Here we report the selective transformation of allenylidene complexes **4** into alkene metathesis catalytic species. In the presence of acid, these (arene)ruthenium−allenylidene complexes in situ rearrange, via alkenylcarbyne intermediates [(η^6-*p*-cymene)RuCl(≡CCH=CR_2)(PR_3)]X_2, into (arene)ruthenium indenylidene derivatives [(η^6-arene)RuCl(ind)(PR_3)]X (eq 1).



(1)

This new acid-promoted process allows the first direct observation of an allenylidene-to-indenylidene rearrangement that brings a new light in allenylidene− and indenylidene−metal complex

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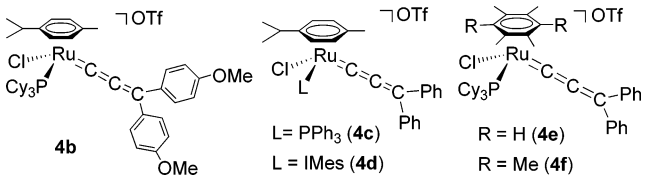
Table 1. Acid-Promoted Cyclooctene Polymerization at Room Temperature[a]

entry	catalyst	ratio[b]	acid[c]	time	yield (%)	$10^{-3}\times M_n$	PDI	% cis	TOF (min^{-1})
1	**4a**	1 000		15 h	95	143	1.9	27	1
2	**4a**	1 000	HBF_4 (5 equiv)	1 min	92	224	1.7	40	920
3	**4a**	1 000	HOTf (5 equiv)	1 min	95	238	1.6	38	950
4	**4a**	10 000	HOTf (5 equiv)	5 min	97	387	1.5	28	1 940
5	**4a**	100 000	HOTf (100 equiv)	5 min	88	857	1.4	35	17 600
6	**4b**	10 000	HOTf (5 equiv)	10 min	73	220	1.8	25	730
7	**4c**	10 000	HOTf (5 equiv)	8 h	25	107	1.9	22	5
8	**4d**	10 000	HOTf (5 equiv)	20 min	90	263	1.9	32	450
9	**4e**	10 000	HOTf (5 equiv)	5 min	92	286	1.6	26	1 840
9	**4f**	1 000	HOTf (5 equiv)	16 h	<5				

[a] 4.5×10^{-3} mol of cyclooctene in 2.5 mL of PhCl. [b] [cyclooctene]/[Ru]. [c] Related to complex.

Chart 2



chemistry and catalysis and shows that indenylidene−ruthenium(arene) complexes are very active catalysts in a variety of alkene metathesis applications. The first elements of this detailed study were previously reported.[22]

Results and Discussion

1. Evidence for Enhancement of Catalytic Activity for ROMP Reactions of Allenylidene−Ruthenium Complexes on Protonation. Preliminary results on cyclooctene polymerization promoted by allenylidene−ruthenium(II) complexes show that the treatment of the initiator [(η^6-*p*-cymene)RuCl(=C=C=CPh_2)(PCy_3)]OTf (OTf = CF_3SO_3) (**4a**) with a strong acid largely increases polymerization rates. Addition of 5 equiv of HBF_4 or HOTf to catalytic solutions of **4a** in chlorobenzene caused the polymerization of 1000 equiv of cyclooctene in 1 min, increasing turnover frequency (TOF) values by 3 orders of magnitude (Table 1, entries 1−3). The in situ-prepared catalytic system is also active with higher monomer loading; thus, it polymerized 10 000 equiv of cyclooctene in 5 min, showing a conversion of 97% corresponding to a TOF of 1940 min^{-1} (entry 4). A tremendous increase of the TOF value to 17 000 min^{-1} was reached when 100 000 equiv of monomer was loaded (entry 5). It was verified that polymerization does not take place with triflic acid in the absence of ruthenium−allenylidene precatalyst.

Slight modifications of the starting allenylidene complex were made by changing substituents on the phenyl groups, [(η^6-*p*-cymene)RuCl{=C=C=C(*p*-OMe-$Ph)_2$}(PCy_3)]OTf (**4b**), the phosphine, [(η^6-*p*-cymene)RuCl(=C=C=CPh_2)(PPh_3)]OTf (**4c**) and [(η^6-*p*-cymene)RuCl(=C=C=CPh_2)(IMes)]OTf (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene) (**4d**), or the η^6-arene ligand, [(η^6-1,2,4,5-tetramethylbenzene)RuCl(=C=C=CPh_2)(PCy_3)]OTf (**4e**) and [(η^6-hexamethylbenzene)RuCl(=C=C=CPh_2)(PCy_3)]OTf (**4f**) (Chart 2). Addition of 5 equiv of triflic acid to solutions of **4b**−**e** promoted the formation of cyclooctenamer as well (entries 6−9). Only precursor **4e** led to results similar to those observed for **4a**, showing that either the use of the less electron-donating phosphine PPh_3 (**4c**) or the introduction of electron-releasing groups in the phenyl rings (**4b**) reduces catalytic activity. The catalytic system generated starting from complex **4d**, which bears a stronger electron-donor ligand instead of PCy_3, presents surprisingly poorer activity. The more strongly coordinated η^6-hexamethylbenzene ligand in **4f** makes it almost inactive.

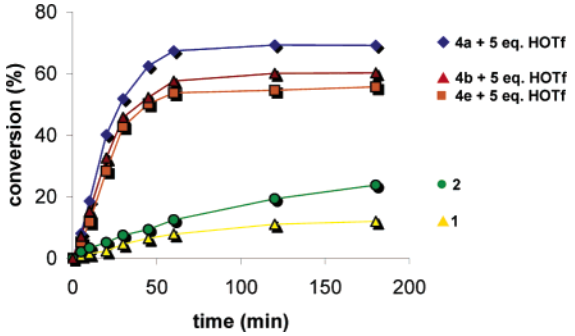


Figure 1. Cyclopentene polymerization monitorized by ^1H NMR experiments at 0 °C.

Due to the high activity presented by these in situ-generated catalysts for ROMP of cyclooctene, polymerization of the less reactive cyclopentene was evaluated. To prevent catalyst decomposition, catalytic assays were carried out at 0 °C. A Schlenk tube was charged with allenylidene complex (**4a**, **4b**, or **4e**), 1000 equiv of cyclopentene (2.33 M), PhCl, and 5 equiv of triflic acid. To compare the catalytic activity, experiments with the well-known stable ruthenium−alkylidene catalysts **1** and **2** were carried out at room temperature. The results are compiled in Figure 1. It is observed that the catalytic activity of the in situ-generated systems from **4a**, **4b**, and **4e** surpasses that of the commercial complexes **1** and **2**. In addition, when 5 equiv of triflic acid was added to solution containing catalyst **2**, even lower yields and TOF were obtained, in agreement with the previous observation that addition of HCl does not improve the activity of pure **2**.[23]

2. Elucidation of the Allenylidene− to Indenylidene−Ruthenium Rearrangement. To understand the nature of the catalytic species generated on addition of acid to ruthenium−allenylidene complexes and control their synthesis, low-temperature NMR studies were performed. It was observed that addition of triflic acid to **4a** provokes the rearrangement of the allenylidene moiety into indenylidene species [(η^6-*p*-cymene)RuCl(ind)(PCy_3)]OTf (**7**) via a dicationic alkenylcarbyne intermediate, [(η^6-*p*-cymene)RuCl(≡CCH=CPh_2)(PCy_3)]$(OTf)_2$ (**6**) (Scheme 1). Figure 2 displays the transformation **4a** → **6** → **7** based on $^{31}P\{^1H\}$ NMR spectra. It is shown that the allenylidene complex **4a** is readily transformed into a new species **6**, which disappears to give **7** in 25 min at −15 °C.

The first step is the protonation of the nucleophilic C_β of the allenylidene ligand of **4a** that takes place at −40 °C. Other ruthenium−alkenylcarbyne complexes have been synthesized by a similar procedure.[14d,24] The $^{13}C\{^1H\}$ NMR spectrum of **6** displays a low-field doublet at 328.1 ppm ($^2J_{P-C}$ = 11 Hz) for the Ru≡C carbon atom. The olefinic proton (δ_H = 7.05)

(22) Castarlenas, R.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4524.

(23) Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153.

(24) (a) Cadierno, V.; Diéz, J.; García-Garrido, S. E.; Gimeno, J. *Organometallics* **2005**, *24*, 3111. (b) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 3980. (c) Bustelo, E.; Jimenez-Tenorio, M.; Meriter, K.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 1903.

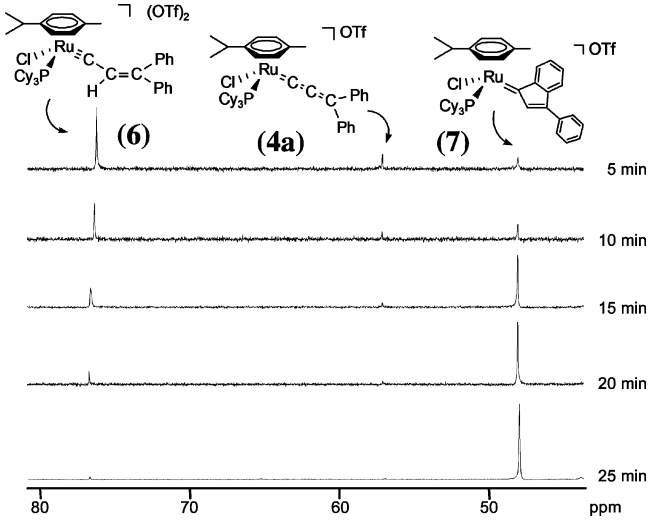
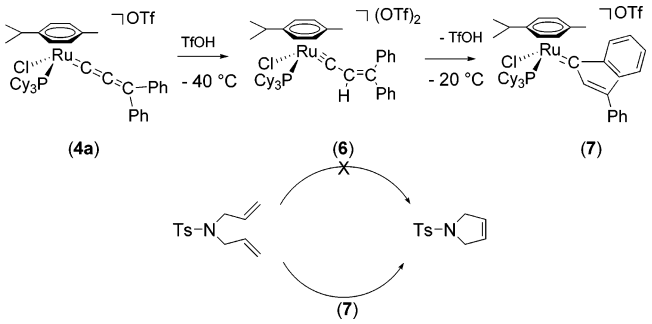


Figure 2. Addition of 2 equiv of triflic acid to **4a** at −15 °C: evolution of $^{31}P\{^1H\}$ NMR spectra as a function of time.

Scheme 1

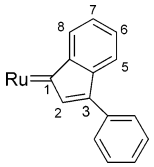


correlates with C_β (130.5 ppm) in a $^1H-^{13}C$ HMQC experiment. More interestingly, the $^1H-^{13}C$ HMBC spectrum displays an interaction between the alkenylcarbyne hydrogen atom and C_γ (193.2 ppm), but no cross-peak is observed with C_α located at the same bond separation. Similar behavior has been observed for the alkenylcarbyne complex $RuCl_3(PPh_3)_2\{\equiv CCH{=}C(Me)_2\}$.[25] Warming the solution to −20 °C leads to the formation of indenylidene derivative **7**, resulting from the *ortho*-phenyl substitution by the electrophilic C_α carbon of **6**, with release of the added triflic acid. Thus, in the dicationic species **6** a stronger contribution of the canonical form **6B** can favor this rearrangement (eq 2).

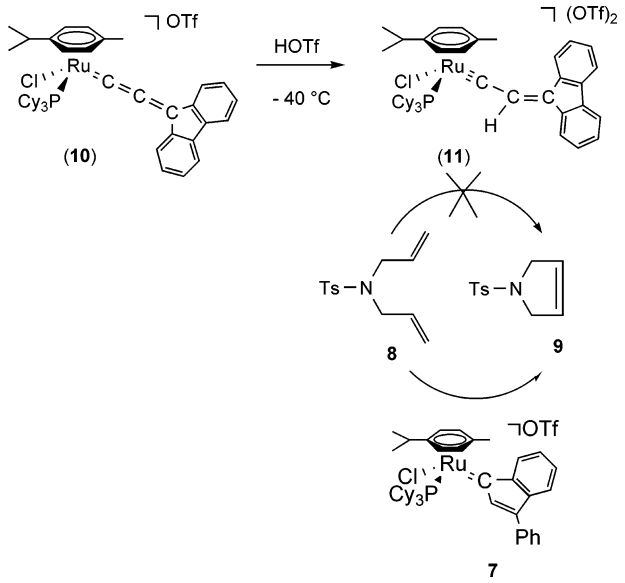
$$[Ru^+{\equiv}C{-}CH{=}CPh_2 \leftrightarrow Ru{=}C^+{-}CH{=}CPh_2] \qquad (2)$$
$$\textbf{(6A)} \qquad\qquad \textbf{(6B)}$$

The $^{13}C\{^1H\}$ NMR spectrum of **7** shows a lower-field doublet ($^2J_{P-C}$ = 10 Hz) at 334.1 ppm corresponding to the Ru=C carbon atom. The ^1H spectrum displays a singlet at 6.88 ppm that correlates with C_2 (143.1 ppm) in a $^1H-^{13}C$ HMQC experiment (Chart 3). The unambiguous presence of the indenylidene ligand is found from analysis of $^1H-^{13}C$ HMBC data. In contrast to the observation for **6**, the olefinic proton correlates with the carbene carbon atom. Indeed, C_α interacts with aromatic proton H_8 (δ_H = 8.33), demonstrating that both atoms were in the vicinity of no more than three bonds, whereas it was six bonds for its alkenylcarbyne precursor **6**. A related

Chart 3



Scheme 2



rearrangement was previously observed from the *trans*-$[Cl(dppm)_2Ru{=}C{=}C{=}C{=}CPh_2]PF_6$ intermediate via *ortho*-phenyl electrophilic substitution, but with the electrophilic C_γ carbon atom.[26] Since our initial communication,[22] related osmium−indenylidene derivatives, characterized by X-ray crystallographic analysis, have been prepared by protonation of allenylidene−osmium complexes.[27]

Previously, it has been shown that both indenylidene[21] and carbyne[28] complexes were able to act as olefin metathesis initiators. To establish which of the derivatives **6** or **7** is the actual precatalyst, RCM of diallyltosylamide (**8**) into 1-tosyl-2,5-dihydropyrrole (**9**), mediated by the catalytic system made from **4a** (2 mol %) and 5 equiv of HOTf, was monitored by NMR experiments. Formation of alkenylcarbyne complex **6** was observed by $^{31}P\{^1H\}$ NMR, but the RCM product **9** was not detected after 1 h at −40 °C. By contrast, warming the solution to 0 °C caused the formation of indenylidene derivative **7**, with the appearance of the RCM product **9**, reaching 99% of conversion in 30 min (Scheme 1).

To corroborate the lack of activity of alkenylcarbyne derivatives, complex $[(\eta^6\text{-}p\text{-cymene})RuCl(\equiv CCH{=}CR_2)(PCy_3)](OTf)_2$ (**11**) (R_2 = 2,2′-biphenyldiyl), bearing a fluorene group on C_γ of the alkenylcarbyne moiety, was prepared by acid treatment of allenylidene $[(\eta^6\text{-}p\text{-cymene})RuCl(=C{=}C{=}CR_2)(PCy_3)]OTf$ (**10**) at −40 °C (Scheme 2). Formation of a new complex **11** is

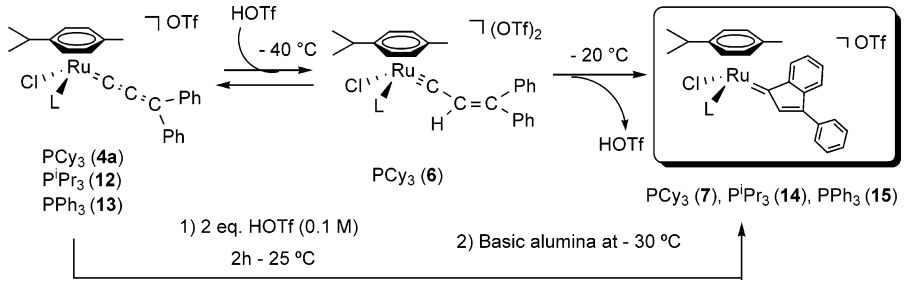
(25) Amoroso, D.; Snelgrove, J. L.; Conrad, J. C.; Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Adv. Synth. Catal.* **2002**, *344*, 757.

(26) (a) Pirio, N.; Touchard, D.; Dixneuf, P. H.; Fettouhi, M.; Ouahab, L. *Angew. Chem. Int. Ed. Engl.* **1992**, *104*, 651. (b) Peron, D.; Romero, A.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 3319.

(27) Asensio, A.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 5787.

(28) (a) Jung, S.; Ilg, K.; Brandt, C. D.; Wolf, J.; Werner, H. *Dalton Trans.* **2002**, 318. (b) Gonzalez-Herrero, P.; Weberndörfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Organometallics* **2001**, *20*, 3672. (c) Stüer, W.; Wolf, J.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3421.

Scheme 3



revealed by the appearance of a new signal at 76.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The $^{13}C\{^1H\}$ NMR spectrum shows a lower-field doublet ($^2J_{P-C}$ = 19.2 Hz) at 327.5 ppm, corresponding to the Ru≡C carbon atom which, similarly to the observation for **6**, does not correlate with the olefinic proton (δ_H = 6.90) in a $^1H-^{13}C$ HMBC experiment. The special structure of **11**, bearing *attached* phenyl groups as substituents on the alkenylcarbyne ligand, inhibits the rearrangement of the allenylidene moiety into an indenylidene species. This was corroborated by the fact that no new species was observed after 4 h at 0 °C. Furthermore, no catalytic activity was observed for alkenylcarbyne derivative **11** on the RCM of **8** into **9** that was promoted by the indenylidene complex **7** (Scheme 2).

3. Isolation of Ruthenium−Indenylidene Derivatives. Even though the in situ-generated catalytic systems obtained by addition of a strong acid to ruthenium−allenylidene derivatives have exhibited high activity in ROMP of cyclooctene at room temperature, it was necessary to operate at 0 °C in order to perform catalytic reactions of less reactive substrates, as complex **7** progressively decomposes at room temperature under these conditions with release of *p*-cymene and [$HPCy_3$]OTf. Decomposition of active species is probably accelerated by the presence of an excess of acid. As we have discovered that triflic acid acts only as a promoter of the allenylidene−indenylidene rearrangement, once this transformation is completed, excess acid could be removed without loss of catalytic activity.[29] On the basis of these observations, the isolation of indenylidene derivatives that should allow acid-free catalytic reactions was attempted (Scheme 3).

A garnet solution of **4a** (300 mg, 0.34 mmol) in 5 mL of CH_2Cl_2 at −60 °C was treated with 60 μL (0.67 mmol) of triflic acid. The solution immediately changed to brown and became dark violet after 2 h at −25 °C. The initial formation of the alkenylcarbyne derivative **6** on protonation of **4a** in equilibrium is highly dependent on the pH of the solution. It was observed that lowering the concentration of triflic acid, by simply increasing the amount of solvent, inhibited the reaction and the allenylidene starting material was recovered. Moreover, higher concentrations of acid led to decomposition of subsequent indenylidene species even at −30 °C. Therefore, an optimal concentration of acid was found to be around 0.1 M and 2 equiv relative to complex **4a**.

After the formation of complex **7** is accomplished, it is mandatory to neutralize the reaction mixture at low temperature. The solution was passed through a cold basic alumina column and eluted with CH_2Cl_2. The solvent was then evaporated below −30 °C, and the residue precipitated in a mixture of cold diethyl ether/pentane. Low-temperature NMR analysis of the isolated brown solid shows signals corresponding to complex **7**.[30] Attempts to obtain monocrystals suitable for X-ray analysis were unsuccessful. A similar experimental procedure was applied to transform the corresponding allenylidene complexes [(η^6-*p*-cymene)RuCl(=C=C=CR_2)(PCy_3)]OTf {R = ^{i}Pr (**12**) and Ph-(**13**)} into indenylidene derivatives [(η^6-*p*-cymene)RuCl(ind)-(PR_3)]OTf {R = ^{i}Pr (**14**) and Ph (**15**)}.

It has been shown that replacement of one phosphine by an NHC ligand in ruthenium−alkylidene initiators improves catalytic activity. Following the experimental procedure developed by Nolan,[14g] the synthesis of complex [(η^6-*p*-cymene)RuCl(=C=C=CPh_2)(IMes)]OTf (**4d**) was accomplished. Attempts to generate the related NHC-indenylidene complex by protonation failed. The higher electron-donor properties of such ligands relative to trialkylphosphines could disfavor the aromatic electrophilic addition because of the enhanced electron density of C_α of the allenylidene moiety. However, in situ protonation of **4d** in the presence of cyclooctene results in the gelification of the solution in 20 min at room temperature (Table 1, entry 8).

4. Olefin Metathesis Reactions Promoted by Acid-Free Indenylidene−Ruthenium Complexes. It has been shown above that in situ-generated indenylidene species are good initiators for olefin metathesis. However, catalytic reactions have to be carried out at 0 °C to prevent catalyst decomposition due to the excess of acid. Isolated indenylidene complexes are able to catalyze alkene metathesis reactions at higher temperatures. Figure 3 shows a comparison between the catalytic performances shown by isolated and in situ-generated indenylidene initiators **7** at room temperature. Both systems display high activity in RCM of diene **8** with low catalyst loading (0.5 mol %). In situ-generated systems display higher initial activity depending on acid concentration. However, conversion is abruptly stopped, probably due to catalyst decomposition. Isolated catalyst **7** presents lower initial performance but it was maintained in the course of the reaction, reaching almost complete conversion in 10 min.

Catalytic activities for ROMP of cyclooctene of indenylidene isolated complexes **7** (PCy_3), **14** (P^iPr_3), and **15** (PPh_3) were studied. Chlorobenzene revealed a better performance than CH_2Cl_2 or toluene, while poorer conversion was observed in THF or diethyl ether. Polymerization results are compiled in Table 2. Complex **7** polymerizes cyclooctene with an extremely low

(29) Previously it has been shown that addition of acid to Grubbs-type systems accelerates the rate of the catalytic reaction. In these cases, acid promotes phosphine decoordination, liberating the 14-electron active species, but does not affect propagating steps. (a) Reference 22. (b) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601.

(30) Due to instability of ruthenium−indenylidene complexes at room temperature, satisfactory elemental analysis could not be obtained.

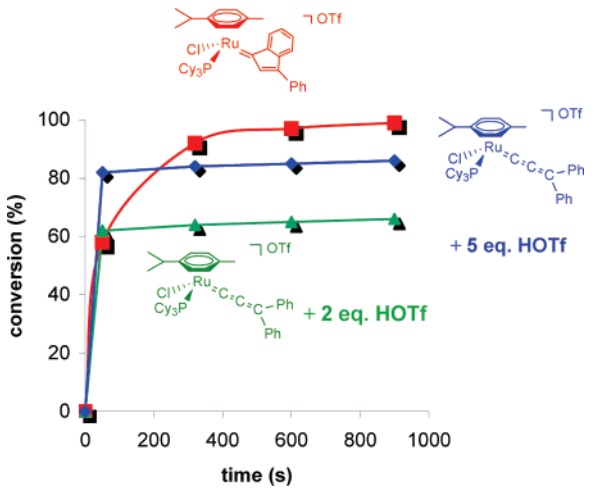


Figure 3. Comparison of catalytic activity in the RCM of **8** between in situ acid-generated and isolated catalysts **7** at room temperature.

Table 2. Cyclooctene Polymerization Catalyzed by Isolated Indenylidene Complexes at Room Temperature[a]

entry	catalyst	ratio[b]	time	yield (%)	$10^{-3}\times M_n$	PDI	TOF (min^{-1})
1	**7**	10 000	1 min	99	549	1.31	9 900
2	**7**	30 000	3 min	92	754	1.35	9 200
3	**7**	100 000	16 h	32	645	1.61	33
4	**14**	10 000	2 min	93	621	1.41	4 650
5	**15**	10 000	16 h	42	387	1.53	4

[a] 4.5×10^{-3} mol of cyclooctene in 2.5 mL of PhCl. [b] [monomer]/[Ru].

catalyst loading (1:30 000) in only 5 min, displaying an impressive TOF of 9200 min^{-1} (entry 2). Activity of **7** diminished when the monomer/ruthenium ratio was increased to 100 000, probably due to decomposition of catalyst by monomer impurities. Indenylidene derivative **14** is a good initiator and presents a slightly lower activity than that of **7**. Poorer conversions are reached with derivative **15**, showing that both electron-donor ability and bulkiness of the phosphine ligand play key roles.

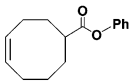
Catalytic activity of complex **7** was evaluated in ROMP of less reactive monomers. It was found that, with Schrock-type initiators [W(=CH^{t}Bu)(O^tBu)$_2$(NAr)], polymerization of cyclopentene takes place at temperatures below −40 °C ([catalyst]:[monomer] = 1:200, 4 h, 95% conversion).[31] At this temperature, complex **7** was able to polymerize in 1 h up to 98% of cyclopentene with an extremely low loading of catalyst (1:10 000), showing even better activity (Table 3, entry 1). However, experiments carried out at room temperature gave rise to initial gelification of the sample, but a progressive decrease of viscosity was observed and no polymer was recovered after treatment of samples, indicating that complex **7** acts also as a depolymerization catalyst.[32] Complex **7** is less active in the ROMP of oxygen-containing monomers like epoxy-5-cyclooctene and cyclooctenylphenyl ester, probably due to the coordination of the polar groups to propagating species.

Isolated indenylidene derivatives are able to catalyze RCM and enyne metathesis reactions of a very large set of products at room temperature (Table 4). An impressive performance was found for RCM of diene **8**, which was completed in only 1 min. To know the applicability of this catalyst for RCM of more complicated substrates, which is of industrial interest, more sterically demanding substrates were tested. In the cases of γ-(**16**) and β-methyl (**17**)-substituted diallyltosylamide, both are smoothly cyclized but 16 h is necessary to transform **17** into **18** (entries 2 and 3).

Catalyst **7** is also active for the rearrangement of enynes into alkenylcycloalkenes by enyne RCM. Transformation of compound **19** into **20** can be used as a simple test to quantify catalyst activity. Only 90 min was necessary to reach 93% yield (entry 4). This catalyst opens access to new compounds of added value and with atom economy. Polyfluorenes are organic electroluminescent materials that have been applied to devices in photonics and optoelectronics.[33] The allyl propargyl fluorene derivative **21** was transformed with catalyst **7** into diene **22** that has potential as a monomer block for the synthesis of polymer-supported chromophores. Different terpenoids with flavor interest, such as compounds derived from (−)-myrtenal (**24**), (−)-menthone (**26**), and citral (**28**), were formed as well in better yield under mild conditions as compared to previous attempts (entries 6−8).[34]

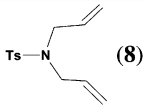
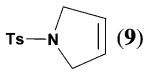
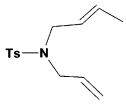
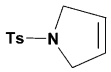
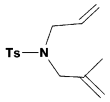
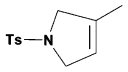
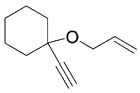
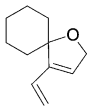
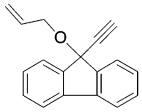
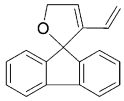
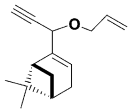
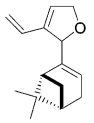
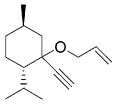
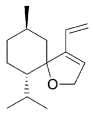
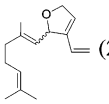
5. New Allenylidene−Metal Precatalyst. The alkene metathesis catalytic activity observed for allenylidene precatalysts motivated us to undertake modifications of the γ-substituents on the allenylidene moiety. The synthesis of various allenylidene complexes was attempted by reaction of the cationic complex [(η^6-*p*-cymene)RuCl(PCy_3)]OTf (**29**) with propargyl alcohols in CH_2Cl_2. Treatment of **29** with 2-phenyl-3-butyn-2-ol led to the allenylidene derivative [(η^6-*p*-cymene)RuCl{=C=C=C(Me)-Ph}(PCy_3)]OTf (**30**), which was isolated at low temperature. The reaction carried out with 1-phenyl-2-butyn-1-ol and 2-methyl-3-butyn-2-ol gave rise to several unidentified products. The more interesting features observed in the $^{13}C\{^1H\}$ NMR spectrum of **30** are two singlets at 288.3 and 169.4 ppm, corresponding to C_α and C_β, respectively, of the allenylidene moiety. A signal corresponding to a methyl group appears at

Table 3. ROMP of Unstrained Monomers Mediated by **7**

entry	substrate	T(°C)	time(h)	yield(%)	$10^{-3}\times M_n$	PDI	TOF (min^{-1})
1[a]		- 40	1	98	76	1.7	163
2[b]		20	16	65	26	1.2	0.7
3[b]		20	16	92	32	1.3	1

[a] 2.5 mL of PhCl. [monomer]/[Ru] = 10 000. [b] 2.5 mL of PhCl. [monomer]/[Ru] = 1000.

Table 4. RCM and Enyne Metathesis Reactions Promoted by **7**[a]

entry	substrate	product	time	yield(%)
1	 (**8**)	 (**9**)	1 min	99
2	 (**16**)		30 min	95
3	 (**17**)	 (**18**)	16 h	65
4	 (**19**)	 (**20**)	90 min	93
5	 (**21**)	 (**22**)	24 h	95
6	 (**23**)	 (**24**)	24 h	72
7	 (**25**)	 (**26**)	24 h	96
8	 (**27**)	 (**28**)	24 h	78

[a] 2.5 mL of PhCl. [monomer]/[Ru] = 50 at room temperature.

33.3 ppm, which correlates with the methyl group ($\delta_H = 2.49$ ppm) in the $^1H-^{13}C$ HMQC experiment, and discards a vinylvinylidene species.[35] Moreover, a strong allenylidene IR band was observed at 1957 cm^{-1}.

It was found that replacing a phenyl group with a methyl group on the allenylidene ligand of **4a** resulted in an increase of the catalytic activity of **30** (Figure 4). After 3 h at room temperature, substrates **8** and **19** were transformed into **9** and **20** in 92 and 85% respectively, whereas catalyst **4a** attained 60 and 70% of final products under the same conditions. However, the performance of catalyst **30** did not reach that displayed by indenylidene **7**.

Catalyst **30** presents good activity for ROMP reactions as well (Table 5). Cyclopentene was polymerized at −40 °C, showing a TOF value of 150 min^{-1}, which is close to that observed for **7** (163 min^{-1}). In the case of cyclooctene, complete gelification of sample was observed in 5 min, but only 63% of polymer was recovered.

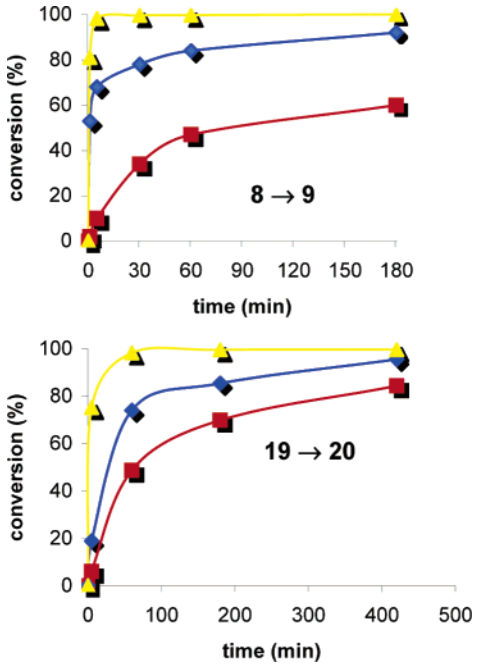


Figure 4. Compared catalytic activity of **4a** (red squares), **7** (yellow triangles), and **30** (blue diamonds) on the transformation of **8** and **19**.

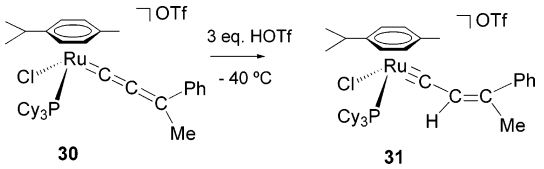
(31) (a) Dounis, P.; Feast, W. J.; Kenwright, A. M. *Polymer* **1995**, *36*, 2787. (b) Schrock, R. R.; Yap, K. B.; Yang, D. C.; Sitzmann, H.; Sita, L. R.; Bazan, G. C. *Macromolecules* **1989**, *22*, 3191.
(32) Polymerization of cyclopentene at −40 °C must be quenched by addition of ethyl vinyl ether and $CHCl_3$ at low temperature. The resulting mixture has to be kept stirring for 1 h at −40 °C and then be allowed to slowly reach room temperature.
(33) (a) Li, J. Y.; Ziegler, A.; Wegner, G. *Chem. Eur. J.* **2005**, *11*, 4450. (b) Wong, W. Y. *Coord. Chem. Rev.* **2005**, *249*, 971. (c) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.
(34) Le Nôtre, J.; Bruneau, C.; Dixneuf, P. *Eur. J. Org. Chem.* **2002**, 3816.
(35) (a) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.

Table 5. ROMP Reactions of Cyclic Alkenes Catalyzed by **30**[a]

entry	substrate	T(°C)	time	yield(%)	$10^{-3} \times M_n$	PDI	TOF (min^{-1})
1		- 40	1 h	90	84	1.6	150
2		20	5 min	63	646	1.5	1260

[a] 2.5 mL of PhCl. [monomer]/[Ru] = 10000.

Scheme 4



Complex **30** may rearrange to a novel methyl-indenylidene intermediate as previously described for its phenyl−phenyl-allenylidene counterpart. Addition of triflic acid to CD_2Cl_2 solutions of **30** at −40 °C gave rise to the formation of the alkenylcarbyne complex [(η^6-*p*-cymene)RuCl{≡C−CH═C(Me)-Ph}(PCy_3)](OTf)$_2$ (**31**) (Scheme 4) as indicated by low-temperature NMR experiments. The most notable feature of **31** is the Ru≡C signal that appears at 332.0 ppp in the $^{13}C\{^1H\}$ NMR spectrum. That signal does not correlate with the olefinic proton (δ_H = 7.12), and a typical five-proton phenyl group is observed in the ^1H NMR spectrum. However, warming the solution to −20 °C led to a mixture of several products that could not be characterized. Complex **31** presents very low alkene metathesis catalytic activity, similar to the other alkenylcarbyne derivatives **6** and **11**.

6. Activation Mechanism for Allenylidene Precatalysts. The ruthenium−allenylidene and precatalysts **4** and **7** are ionic 18-electron species. To become an active catalytic species they must be coordinatively unsaturated in order to allow a substrate to enter the coordination sphere of the metal. Usually catalytic species have 16 or even 14 electrons for some olefin metathesis initiators. To generate vacant sites a ligand must decoordinate from **7**. There are two candidates, the phosphine or the η^6-bound *p*-cymene ligand. Grubbs and co-workers proposed that decoordination of one phosphine is the activation step for catalysts **1** and **2**.[9] In addition, acid treatment of Grubbs catalysts favors decoordination of the phosphine. In that case an electron-releasing ligand remains bound to the ruthenium atom, stabilizing the metallacycle intermediate.

On the hypothesis that the phosphine ligand decoordinates from our initiators **7**, no other electron-releasing ligand would stabilize the formation of a metallacycle intermediate. The nature of the phosphine (PCy_3, P^iPr_3, and PPh_3) strongly modifies the catalytic activity of indenylidene complexes and thus supports the hypothesis that the presence of a phosphine ligand is essential in the propagation species. Moreover, it has been previously described that the *p*-cymene ligand is a weak ligand that could be easily released. Indeed, previous activation of allenylidene catalyst by UV light improves catalytic activity because of decoordination of an arene ligand.[16b,17b] In the catalytic transformation **8** → **9** by complexes **4** and **7**, the free p-cymene is always observed in the initial step of the reaction by ^1H NMR spectroscopy and gas chromatography.

These observations suggest the following mechanism (Figure 5). The first step is the rearrangement of the allenylidene moiety into an indenylidene species. Subsequent decoordination of the η^6-bound arene ligand generates an unsaturated species that could be stabilized by the counterion. The resulting 14-electron initiators could enter into a Chauvin cycle for promoting olefin metathesis reactions.

First Step: Rearrangement. The allenylidene ligand is transformed into an indenylidene group via an aromatic electrophilic substitution which is favored by the electrophilicity of the C_α carbon atom. Electron-releasing ancillary ligand L should disfavor this rearrangement and thus the catalyst precursor formation. This inhibition to form the indenylidene group accounts for the lower catalytic activity found for complex **4d** that bears an electron-releasing imidazolylidene ligand. Addition of acid may favor this step due to the formation of alkenylcarbyne species which possesses a more electrophilic carbon atom than the allenylidene moiety.

Second Step: Generation of Active Species. As discussed previously, decoordination of η^6-bound arene is the most plausible way to generate species that are coordinatively unsaturated. It is obvious that the stronger steric interaction between the arene ligand and the indenylidene group, with respect to that of the allenylidene group, may favor the arene decoordination. An increase in the stability of the arene−ruthenium bond causes a decrease in catalytic performance from **4a** (*p*-cymene) to **4e** (tetramethylbenzene) and **4f** (hexamethylbenzene). Decoordination of the *p*-cymene ligand generates a highly unsaturated 12-electron species that is likely stabilized by the coordination ability of the triflate ligand. It explains the differences observed in catalytic activity on counterion variation.[13b] These intermediates must be protected by an ancillary ligand to prevent deactivation by dimerization of the carbene ligand. Thus, bulky ligands such as NHC may favor this step whereas phosphines need to have a large cone angle.

Third Step: Propagation. Once ruthenium−indenylidene *p*-cymene-free species are generated, they can enter into the catalytic cycle. Metallacyclobutane stabilization is favored by the electron-releasing capability of the ancillary ligands. Thus, NHC is the most favorable ligand and the less-electron-donating PPh_3 is the least favorable group. Based on experimental results, the best compromise for the overall activity is provided by PCy_3, which has electron-donating capability between those of imidazolylidene and PPh_3 groups.

Conclusion

By contrast to previous works showing that (arene)ruthenium−allenylidene catalysts are active catalysts for alkene metathesis reactions, we have now observed the direct rearrangement of the allenylidene−metal complex into an inde-

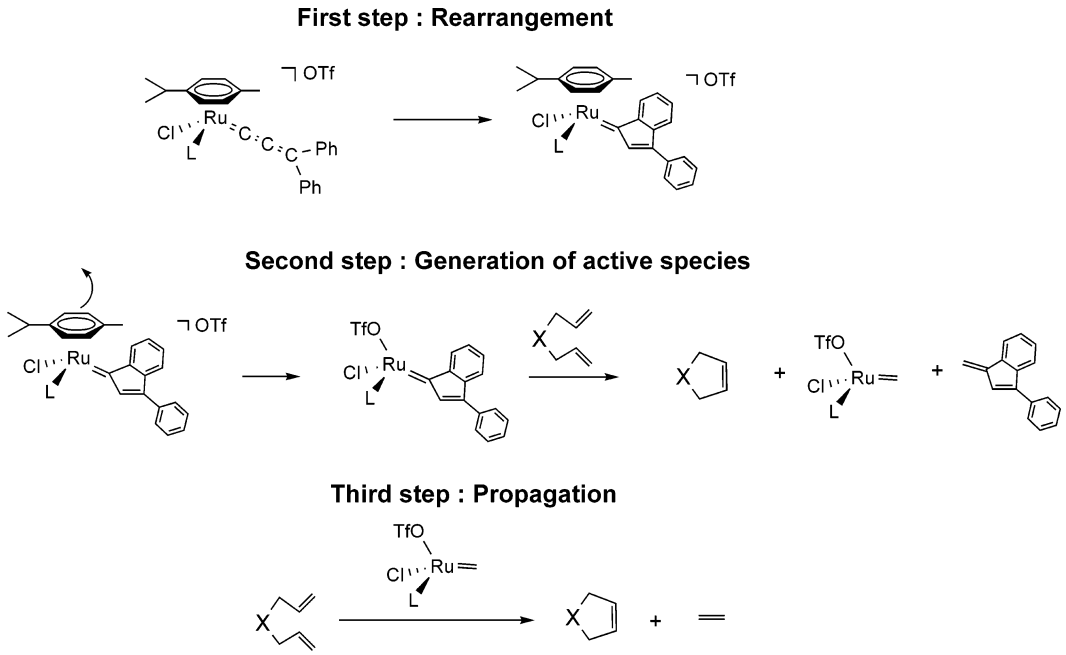


Figure 5. Activation mechanism for allenylidene precatalysts.

nylidene−metal derivative. This rearrangement was previously questioned but never directly observed. It is now established that this acid-promoted reaction involves the electrophilic alkenylcarbyne−ruthenium intermediate formation. The above results show that in situ-generated (arene)ruthenium−indenylidene intermediates are extremely active in ring-opening metathesis polymerization reactions and that the isolated derivatives show even improved catalytic activity for the ring-closing metathesis of a variety of dienes and enynes.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk tube techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use. Starting complexes [(η^6-*p*-cymene)RuCl(PCy$_3$)][X],[13b] [(η^6-*p*-cymene)RuCl(=C=C=CAr$_2$)(PR$_3$)][X],[13b] and (η^6-*p*-cymene)RuCl$_2$(IMes)[14g] and organic products **16**,[13a] **17**,[10d] and (**19**, **23**, **25**, **27**)[34] were synthesized as previously described in the literature. Cyclooctene and cyclopentene were distilled from powdered NaOH and stored under argon with 4-Å molecular sieves. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AM 300 WB spectrometer, and chemical shifts are expressed in parts per million (ppm) downfield from Me$_4$Si. ^{13}C{^{1}H} NMR spectra were recorded at 75.4 MHz, and chemical shifts are expressed in ppm downfield from Me$_4$Si. ^{31}P{^{1}H}NMR spectra were recorded at 121.4 MHz, and chemical shifts are expressed in ppm downfield from 85% H$_3$PO$_4$. Coupling constants, *J*, are given in hertz. Samples for IR spectra were prepared as Nujol mulls on polyethylene sheets.

Preparation of [(η^6-*p*-Cymene)RuCl(=C=C=CPh$_2$)(IMes)][OTf] (4d). A light-protected orange solution of (η^6-*p*-cymene)RuCl$_2$(IMes) (500 mg, 0.82 mmol) in 20 mL of CH$_2$Cl$_2$ was treated with 211 mg (0.82 mmol) of AgOTf and stirred for 30 min. The resulting violet suspension was filtered through Celite, and 190 mg (0.91 mmol) of 1,1-diphenyl-2-propyn-1-ol was added. After 4 h at room temperature, the resulting dark red solution was evaporated to dryness, washed three times with a mixture of pentane (5 mL)/diethyl ether (3 mL), and then dried under vacuum (485 mg, 65% yield). IR (Nujol, cm^{-1}): ν(C=C=C) 1968, ν_a(SO$_3$) 1261 (s); ν_a(CF$_3$) 1148 (s); ν_s(SO$_3$) 1027 (s); δ_a(SO$_3$) 638 (s). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.1−7.9 (m, 16 H, H$_{Ph}$), 5.67, 5.61, 5.37, and 5.04 (all d, J_{H-H} = 9.6 Hz, 4 H, η^6-*p*-cymene), 3.2 (m, 1 H, ^{i}Pr), 2.5−1.2 (27 H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ 284.1 (br, Ru=C), 188.7 (s, Ru=C=*C*), 173.2 {s, Ru−C(Imes)}, 160.5 (s, Ru=C=C=*C*), 141.6, 141.4, 140.7, 137.2, and 137.1 (all s, C$_q$), 134.2, 133.1, 132.2, 130.5, 129.8, 129.6, and 128.3 (s, C$_{Ph}$ + Imes), 126.2 and 125.2 (both s, C$_{p-cymene}$), 120.2 (q, J_{C-F} = 319.8 Hz, CF$_3$), 105.4, 104.2, 94.2, and 92.4 (all s, C$_{p-cymene}$), 31.5 (s, CH^{i}Pr), 23.9, 23.0, 21.0, 20.8, 18.6, 18.4, and 17.2 (all s, CH$_3$).

Preparation of [(η^6-*p*-Cymene)RuCl(≡C−CH=CPh$_2$)(PCy$_3$)](OTf)$_2$ (6). A garnet solution of **4a** (40 mg, 0.045 mmol) in 0.5 mL of CD$_2$Cl$_2$ in an NMR tube under an argon atmosphere at 233 K was treated with 5 μL (0.056 mmol) of triflic acid. The color changed immediately to dark orange, and after the NMR tube was sealed under an argon atmosphere, measurements were made. ^{1}H NMR (CD$_2$Cl$_2$, 233 K): δ 8.12 (vt, J_{H-H} = 7.0 Hz, 2 H, H$_{m-Ph}$), 7.8−7.3 (m, 6 H, H$_{Ph}$), 7.05 (s, 1 H, Ru≡C−CH=), 6.92 (vt, J_{H-H} = 7.5 Hz, 2 H, H$_{m-Ph}$), 6.75 and 6.61 (both d, J_{H-H} = 6.0 Hz, 4 H, η^6-*p*-cymene), 2.9−2.6 (m, 4 H, ^{i}Pr and PCH), 2.28 (s, 3 H, CH$_3$), 2.1−0.9 (m, 36 H, Cy and ^{i}Pr). ^{13}C{^{1}H} NMR + DEPT, HMQC and HMBC (CD$_2$Cl$_2$, 233 K): δ 328.1 (d, J_{C-P} = 11 Hz, Ru≡C), 193.2 (s, CH=*C*Ph$_2$), 140.5 and 137.6 (both s, C$_{ipso-Ph}$), 136.0, 134.8, 134.2, 130.3, 129.4, and 127.8 (all s, C$_{ph}$), 130.5 (s, Ru≡C−*C*H=), 128.2 and 125.8 (both s, C$_{ipso-p-cymene}$), 120.4 (q, J_{C-F} = 320.0 Hz, CF$_3$), 111.8, 108.7 (both s, C$_{p-cymene}$), 33.3 (s, CH^{i}Pr), 31−24 (br, Cy), 25.1, 22.2 (s, CH$_{3-}{}^i$Pr), 19.9 (s, CH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 233 K): δ 78.6 (s).

Preparation of [(η^6-*p*-Cymene)RuCl(ind)(PCy$_3$)]OTf (7). A garnet solution of **4a** (300 mg, 0.34 mmol) in 5 mL of CH$_2$Cl$_2$ at 213 K was treated with 60 μL (0.67 mmol) of triflic acid. The solution immediately changed to brown and became dark violet after 2 h at 248 K. The solution was then cooled to 193 K and, after addition of 15 mL of CH$_2$Cl$_2$, was stirred with 4 g of aluminum oxide, activated basic, Brockmann I for 15 min. The product was filtered off, and the alumina was washed two times with 10 mL of CH$_2$Cl$_2$. The resulting dark purple solution was evaporated to dryness below 243 K (it may take a long time). The bright brown-violet solid was washed three times at low temperature with a mixture of pentane (5 mL)/diethyl ether (1 mL) and dried under vacuum. A brown solid was obtained (250 mg, 83% yield). IR (Nujol, cm^{-1}): ν_a(SO$_3$) 1261 (s); ν_a(CF$_3$) 1146 (s); ν_s(SO$_3$) 1032 (s); δ_a(SO$_3$) 639 (s).^{1}H NMR (CD$_2$Cl$_2$, 233 K): δ 8.33 (m, 1 H, H$_{8-ind}$), 7.84 (d, J_{H-H} = 7.5 Hz, 2 H, H$_{o-Ph}$), 7.75 (t, J_{H-H} = 7.5 Hz, 1 H, H$_{p-Ph}$), 7.60 (vt, J_{H-H} = 7.5 Hz, 2 H, H$_{m-Ph}$), 7.42 (m, 2 H, H$_{7-ind}$ and H$_{6-ind}$), 7.13 (m, 1 H, H$_{5-ind}$), 6.88 (s, 1 H, Ru=C−CH=), 6.36,

6.31, 6.19, and 6.15 (all d, 4 H, J_{H-H} = 6.0 Hz, η^6-*p*-cymene), 2.83 (m, 1 H, ^{i}Pr), 2.78 (m, 3 H, PCH), 2.31 (s, 3 H, CH_3), 2.1−0.9 (m, 36 H, Cy and ^{i}Pr). $^{13}C\{^1H\}$ NMR + DEPT, HMQC, and HMBC (CD_2Cl_2, 233 K): δ 334.1 (d, J_{C-P} = 10 Hz, Ru=C), 154.6 (s, C_{3-ind}), 146.8 (s, C_{9-ind}), 143.1 (d, J_{C-P} = 2 Hz, C_{2-ind}), 136.5 (s, C_{4-ind}), 134.7 (s, C_{7-ind}), 133.4 (s, C_{8-ind}), 132.7 (s, C_{6-ind}), 132.5 (s, C_{p-Ph}), 131.7 (s, $C_{ipso-Ph}$), 130.0 (s, C_{m-Ph}), 127.8 (s, C_{o-Ph}), 126.3 and 125.3 (both s, $C_{ipso-p-cymene}$), 121.2 (s, C_{5-ind}), 120.4 (q, J_{C-F} = 320.0 Hz, CF_3), 103.6 and 99.7 (both s, $C_{p-cymene}$), 33.8 (s, CH^iPr); 30−24 (br, Cy); 24.2 and 22.8 (both s, $CH_{3-}{}^iPr$); 19.6 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ 48.3 (s).

Preparation of [(η^6-*p*-Cymene)RuCl{=C=C=C($C_{12}H_8$)}(PCy_3)][OTf] (10). An orange solution of **29** (300 mg, 0.43 mmol) in 10 mL of CH_2Cl_2 at 253 K was treated with 96 mg (0.47 mmol) of 9-ethynyl-9-fluorenol. The solution was kept stirring for 1 h, and then the solvent was removed under vacuum at 253 K. The resulting violet solid was washed with a mixture of pentane (5 mL)/diethyl ether (1 mL) and dried under vacuum. IR (Nujol, cm^{-1}): ν(C=C=C) 1963, $\nu_a(SO_3)$ 1265 (s); $\nu_a(CF_3)$ 1153 (s); $\nu_s(SO_3)$ 1031 (s); $\delta_a(SO_3)$ 637 (s). ^1H NMR (CD_2Cl_2, 243 K): δ 7.7−7.1 (m, 8 H, H_{Ph}), 6.74, 6.68, 6.21, 6.13 (4 H, η^6-*p*-cymene), 2.62 (m, 1 H, ^{i}Pr), 2.32 (m, 3 H, PCH), 2.1−0.9 (m, 36 H, Cy and CH_3). $^{13}C\{^1H\}$ NMR + DEPT, HMQC and HMBC (CD_2Cl_2, 243 K): δ 291.4 (d, J_{C-P} = 21.9 Hz, Ru=C), 195.5 (s, Ru=C=*C*), 159.8 (s, Ru=C=C=*C*), 146.8, 146.1, 141.5, and 139.3 (all s, C_q), 135.5, 130.1, 129.7, and 128.6 (s, C_{Ph}), 122.0 and 120.3 (both s, $C_{p-cymene}$), 120.2 (q, J_{C-F} = 319.8 Hz, CF_3), 108.5, 103.0, 96.2, and 98.9 (all s, $C_{p-cymene}$), 32.2 (s, CH^iPr); 24.3 and 22.6 (both s, $CH_{3-}{}^iPr$); 19.2 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 61.1 (s).

Preparation of [(η^6-*p*-Cymene)RuCl(≡C−CH=C($C_{12}H_8$)(PCy_3)][OTf (11). A violet solution of **10** (50 mg, 0.06 mmol) in 0.5 mL of CD_2Cl_2 in an NMR tube under an argon atmosphere at 233 K was treated with 15 μL (0.17 mmol) of HSO_3CF_3. ^1H NMR (CD_2Cl_2, 233 K): δ 8.2−7.1 (m, 12 H, H_{Ph}, η^6-*p*-cymene), 6.90 (s, Ru≡CCH), 2.81 (m, 1 H, ^{i}Pr), 2.31 (m, 3 H, PCH), 2.1−0.9 (m, 39 H, Cy and CH_3). $^{13}C\{^1H\}$ NMR, HMQC, and HMBC (CD_2Cl_2, 233 K): δ 327.5 (d, J_{C-P} = 19.2 Hz, Ru≡C), 182.6 (s, Ru≡C−CH=*C*), 140.3, 139.3, 138.2, and 135.8 (all s, C_q), 132.1, 131.6, 131.2, 130.4, 129.6, 128.8, 128.2, and 127.6 (s, C_{Ph}), 125.2 and 123.3 (both s, $C_{p-cymene}$), 120.2 (q, J_{C-F} = 320.2 Hz, CF_3), 115.2, 113.8, 112.4, and 109.3 (all s, $C_{p-cymene}$), 31.0 (s, CH^iPr); 25.6 and 24.2 (both s, $CH_{3-}{}^iPr$); 20.4 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ 76.0 (s).

Preparation of [(η^6-*p*-Cymene)RuCl(ind)(P^iPr_3)]OTf (14). This complex was prepared as described for **7** starting from 300 mg (0.39 mmol) of **12** and 60 μL (0.67 mmol) of triflic acid (250 mg, 83% yield). ^1H NMR (CD_2Cl_2, 243 K): δ 8.21 (m, 1 H, H_{8-ind}), 8.1−6.9 (8 H, Ph), 6.92 (s, 1 H, H_{2-ind}), 6.39, 6.30, 6.18, and 6.11 (all d, 4 H, J_{H-H} = 6.0 Hz, η^6-*p*-cymene), 2.79 (m, 1 H, ^{i}Pr), 2.2 (m, 6 H, ^{i}Pr, CH_3), 1.9 (m, 24 H, ^{i}Pr). $^{13}C\{^1H\}$ NMR + DEPT (CD_2Cl_2, 243 K): δ 333.2 (br, Ru=C), 155.0 (s, C_{3-ind}), 147.0 (s, C_{9-ind}), 142.5 (s, C_{2-ind}), 136.6 (s, C_{4-ind}), 133.4 (s, C_{7-ind}), 132.6 (s, C_{8-ind}), 131.2−120.3 (C_{Ph}, C_{5-ind}, C_{6-ind}, CF_3), 121.0 and 116.9 (both s, $C_{p-cymene}$), 104.8, 101.2, 99.8, and 97.2 (all s, $C_{p-cymene}$), 31.4 (s, CH^iPr); 25.9 (s, PCH), 22.2, 19.3, and 18.9 (all s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 54.2 (s).

Preparation of [(η^6-*p*-Cymene)RuCl(ind)(PPh_3)]OTf (15). This complex was prepared as described for **7** starting from 300 mg (0.36 mmol) of **13** and 60 μL (0.67 mmol) of triflic acid (270 mg, 90% yield). ^1H NMR (CD_2Cl_2, 243 K): δ 8.13 (m, 1 H, H_{8-ind}), 8.1−6.9 (27 H, Ph, η^6-*p*-cymene), 6.41 (s, 1 H, H_{2-ind}), 2.59 (m, 1 H, ^{i}Pr), 2.10 (s, 3 H, CH_3), 1.9 (br, 6 H, ^{i}Pr). $^{13}C\{^1H\}$ NMR + DEPT, HMQC, and HMBC (CD_2Cl_2, 243 K): δ 336.1 (d, J_{C-P} = 8 Hz, Ru=C), 154.1 (s, C_{3-ind}), 142.9 (s, C_{2-ind}), 142.0 and 137.3 (both s, C_{4-ind} and C_{9-ind}), 132.3 (s, C_{7-ind}), 131.8 (s, C_{8-ind}), 129.8−120.3 (C_{Ph}, C_{5-ind}, C_{6-ind}, $C_{p-cymene}$, CF_3), 114.2, 113.8 (both s, $C_{p-cymene}$), 32.5 (s, CH^iPr); 25.1 and 23.6 (both s, $CH_{3-}{}^iPr$); 19.4 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 42.1 (s).

Preparation of 9-(Allyloxy)-9-ethynyl-9*H*-fluorene (21). To a solution of NaH (210 mg, 90% purity, 8.33 mmol) in 40 mL of a 1:1 mixture of DMSO and THF at 0 °C was added 1.43 g (6.93 mmol) of 9-ethynyl-9*H*-fluoren-9-ol. After the mixture was stirred for 15 min at 0 °C and 45 min at room temperature, 0.7 mL (8.33 mmol) of allyl bromide was added, and the mixture was kept stirring overnight. The mixture was then hydrolyzed with water, extracted with heptane, dried with $MgSO_4$, and concentrated under vacuum. Further purification by column chromatography (heptane−diethyl ether 8:2) yielded a yellow oil (1.7 g, 98%). ^1H NMR ($CDCl_3$, 293 K): δ 7.8−7.3 (m, 8 H, Ph), 5.85 (m, 1 H, C*H*=CH_2), 5.14 (m, 2 H, CH=C*H*$_2$), 3.72 (m, 2 H, C*H*$_2$-CH=CH_2), 2.53 (s, 1 H, −C≡CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 145.1 and 140.3 (C_{ipso}−Ph), 135,2 (*C*H=CH_2), 130.2, 127.3, 125.3, and 120.9 (C_{Ph}), 116.2 (OCH_2), 82.3 and 72.8 (C≡CH).

Preparation of 13-Vinyl-9,9′-(2,5-dihydrofuran)-9*H*-fluorene (22). A solution of **7** (4 mg, 0.042 mmol) in 3 mL of chlorobenzene under an argon atmosphere was treated with **21** (51 mg, 0,21 mmol), and the mixture was kept stirring for 16 h at room temperature. The solution was then evaporated, and the crude product was purified by column chromatography (heptane−diethyl ether 8:2) (51 mg, 98% yield). ^1H NMR ($CDCl_3$, 293 K): δ 7.9−7.1 (m, 8 H, Ph), 6.34 (s, 1 H, OCH_2−C*H*=C), 6.03 (dd, J_{H-H} = 10.4 and 6.9 Hz, 1 H, C*H*=CH_2), 5.02 (s, 2H, OCH_2), 4.67 (d, J_{H-H} = 9.9 Hz, 1 H, CH=C*H*$_2$), 4.46 (d, J_{H-H} = 10.4 Hz, 1 H, CH=C*H*$_2$).

Preparation of [(η^6-*p*-Cymene)RuCl{=C=C=C(Me)Ph}(PCy_3)][OTf (30). An orange solution of **29** (200 mg, 0.284 mmol) in 10 mL of CH_2Cl_2 at room temperature was treated with 50 mg (0.340 mmol) of 2-phenyl-3-butyn-2-ol. The solution was kept only 1 min at room temperature and then cooled to 253 K for 2 h. The brown solution was evaporated to dryness, washed three times with pentane (6 mL)/ether (1 mL) below 253 K, and dried in a vacuum. IR (Nujol, cm^{-1}): ν(C=C=C) 1957, $\nu_a(SO_3)$ 1263 (s); $\nu_a(CF_3)$ 1148 (s); $\nu_s(SO_3)$ 1029 (s); $\delta_a(SO_3)$ 638 (s). ^1H NMR (CD_2Cl_2, 243 K): δ 8.23 (d, J_{H-H} = 7.4 Hz, 2 H, H_{o-Ph}), 7.82 (t, J_{H-H} = 7.4 Hz, 1 H, H_{p-Ph}), 7.53 (vt, J_{H-H} = 7.4 Hz, 2 H, H_{p-Ph}), 6.71 and 6.65 (both d, J_{H-H} = 6.0 Hz, 2 H, η^6-*p*-cymene), 6.11 and 6.07 (both d, J_{H-H} = 6.6 Hz, 2 H, η^6-*p*-cymene), 2.85 (m, 1 H, ^{i}Pr), 2.66 (m, 3 H, PCH), 2.49 {s, 3 H, =C(C*H*$_3$)Ph}, 2.23 (s, 3 H, CH_3), 2.1−0.9 (m, 36 H, Cy and ^{i}Pr). $^{13}C\{^1H\}$ NMR + DEPT, HMQC, and HMBC (CD_2Cl_2, 243 K): δ 288.3 (d, J_{C-P} = 20 Hz, Ru=C), 169.4 (s, Ru=C=*C*), 141.5 and 135.1 (both s, C_{quat}), 130.5, 129.5, and 128.2 (all s, C_{Ph}), 122.7 and 118.4 (both s, $C_{ipso-p-cymene}$), 120.6 (q, J_{C-F} = 320.0 Hz, CF_3), 107.1, 102.3, 95.5, and 94.9 (all s, $C_{p-cymene}$), 33.3 (s, C(Ph)*C*H$_3$), 32.3 (s, CH^iPr), 29.5−24.5 (br, Cy), 24.1, 19.8, and 18.5 (all s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 57.6 (s).

Preparation of [RuCl(η^6-*p*-Cymene){≡C−CH=C(Me)Ph}(PCy_3)][$(OTf)_2$ (31). An orange solution of **30** (40 mg, 0.048 mmol) in 0.5 mL of CD_2Cl_2 in an NMR tube under an argon atmosphere at 213 K was treated with 14 μL (0.156 mmol) of triflic acid. ^1H NMR (CD_2Cl_2, 243 K): δ 8.13 (d, J_{H-H} = 7.0 Hz, 2 H, H_{o-Ph}), 7.91 (t, J_{H-H} = 7.0 Hz, 1 H, H_{p-Ph}), 7.6−7.3 (m, 6 H, η^6-*p*-cymene, H_{p-Ph}), 7.12 (s, 1 H, Ru≡CCH), 3.11 {s, 3 H, =C(C*H*$_3$)Ph}, 2.82 (m, 1 H, ^{i}Pr), 2.54 (m, 3 H, PCH), 2.23 (s, 3 H, CH_3), 2.1−0.9 (m, 36 H, Cy and ^{i}Pr). $^{13}C\{^1H\}$ NMR + DEPT, HMQC, and HMBC (75.4 MHz, CD_2Cl_2, 243 K): δ 332.0 (br, Ru≡C), 195.6 (s, CH=*C*(Me)Ph), 140.5 and 138.3 (s, $C_{ipso-Ph}$), 131.6, 130.5, and 130.1 (all s, C_{Ph}), 126.6 (s, Ru≡C−*C*H=), 126.0 and 125.3 (both s, $C_{ipso-p-cymene}$), 120.2 (q, J_{C-F} = 318.3 Hz, CF_3), 121.6,120.8, 118.6, and 117.4 (all s, $C_{p-cymene}$), 33.7 (s, C(Ph)-*C*H$_3$), 33.1 (s, CH^iPr), 29.5−25.5 (br, Cy), 22.1, 20.2, 20.0 (all s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 75.7 (s).

General Procedure for the Polymerization of Cycloolefins Using in Situ-Prepared Catalyst. Complex **4a** (8 mg, 9 mmol) was dissolved in PhCl (0.5 mL) at 253 K, and 4 μL (45 mmol) of triflic acid was added. After 30 min at this temperature, the desired amount of freshly prepared catalyst was transferred to a vessel at the chosen temperature containing PhCl (2.5 mL) and monomer (500 mg; 4.5 mmol of

cyclooctene, 1.46 M; 7.3 mmol of cyclopentene, 2.33 M). The same procedure was carried out with isolated complex **7** (9 mmol) in PhCl (2.5 mL) at room temperature. The resulting viscous mixture was dissolved with $CHCl_3$ containing 0.1% of 2,6-di-*tert*-butyl-4-methylphenol (BHT; 20 mL) and vinyl ethyl ether (0.3 mL). This solution was poured into methanol (300 mL) to precipitate the polymer, which was collected by filtration, dried under vacuum, and characterized by ^1H and ^{13}C NMR. Average molecular weights were determined using gel permeation chromatography (GPC) calibrated with polystyrene standards.

General Procedure for the Ring-Closing Metathesis of Dienes or Enynes Using Isolated Catalyst 7. The substrate (0.56 mmol) was added to a solution of complex **7** (10 mg, 11.25×10^{-2} mmol, S/Ru = 50) in dry PhCl (2.5 mL). The progress of the reaction was monitored by gas chromatography. After evaporation of PhCl, the products were isolated by column chromatography on silica gel using mixtures of heptane and diethyl ether as eluents and then characterized by ^1H, ^{13}C NMR and GC/MS analysis.

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