Rate Studies and Mechanism of Ring-Closing Olefin Metathesis Catalyzed by Cationic Ruthenium Allenylidene Arene Complexes

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Received June 26, 2003

The ring-closing metathesis reaction of *N*,*N*-diallyltosylamide (**2**) catalyzed by [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]X (X = OTf (CF_3SO_3) (**1**), PF_6, BF_4, SbF_6) and by [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=C(*p*-Y-C_6H_4)$_2$]OTf (Y = MeO, Cl, F) complexes has been monitored in situ by ^{1}H NMR, in benzene-d_6 and in dichloromethane-d_2, in the temperature range 33−58 °C. The reaction proceeds selectively to form *N*-tosyl-2,5-dihydropyrrole (**3**), in the case of complexes [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]X (X = OTf, PF_6), under thermal activation, while lower reactivity and selectivity are exhibited by the other complexes. Evidence is given for an activation step leading to the catalytic species. Under pseudo-first-order conditions, the metathesis reaction catalyzed by complex **1** is first-order in the diallylic substrate in benzene-d_6 above 50 °C when the propagation step is slower than the activation of the catalytic species. The reaction is zero-order in substrate at lower temperatures when the activation of the ruthenium complex is slower than the ring-closing metathesis process and faster in benzene-d_6 than in dichloromethane-d_2. The presence of added *p*-cymene does not inhibit the reactivity, while inhibition occurs in the presence of added PCy_3. In the latter case, the substrate is converted slowly into an isomeric product. When appropriate, the behavior of complex **1** as precatatyst is compared with that of other catalytic systems. ^{1}H NMR, FT-IR, and UV−visible analyses indicate that the activation process of complex **1** is characterized by an intramolecular transformation of the ruthenium-allenylidene group into the corresponding ruthenium-phenylindenylidene moiety.

Introduction

Olefin metathesis has emerged as a powerful tool for the formation of carbon−carbon double bonds, due to the introduction of well-defined and functional-group-tolerant catalysts.[1] In particular, the ruthenium complexes [$RuCl_2(PCy_3)_2$(=CHR)] (Cy = cyclohexyl) and the novel generation of N-heterocyclic carbene derivatives [$RuCl_2$(NHC)(PCy_3)(=CHR)] (NHC = N-heterocyclic carbene) or related compounds have found extensive applications in organic chemistry.[1,2] The metal alkylidene group (Ru=CHR) of these complexes offers a direct access into the catalytic cycle by interaction with the olefin substrate and formation of a four-membered metallacycle species, which is considered to be a key intermediate in the olefin metathesis process.[3] The mechanism of the reaction has been the subject of several investigations carried out by a variety of techniques, including rate studies,[4] thermochemistry,[5] mass spectrometry,[6] and computational modeling,[7] with the intention to disclose the intimate features of the process as well as to aid the design and use of superior catalysts

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(1) (a) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(2) (a) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546. (b) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954. (c) Arisawa, M.; Terada, Y.; Nakagawa, M.; Nishida, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4732. (d) Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4038. (e) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543. (f) Delaude, L.; Demonceau, A.; Noels, A. F. *Chem. Commun.* **2001**, 986. (g) Randl, S.; Gessler, S.; Wakamatsu, H.; Blechert. *Synlett* **2001**, 430.

(3) Hérisson, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.

(4) (a) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887. (b) Ulman, M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2484. (c) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758. (d) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202. (e) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749.

(5) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375.

(6) (a) Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 2685. (b) Adhlart, C.; Volland, M. A. O.; Hofmann, P.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 3306. (c) Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204. (d) Volland, M. A. O.; Adlhart, C.; Kiener, C. A.; Chen, P.; Hofmann, P. *Chem. Eur. J.* **2001**, *7*, 4621.

(7) (a) Aagaard, O. M.; Meier, R. J.; Buda, F. *J. Am. Chem. Soc.* **1998**, *120*, 7174. (b) Hansen, S. M.; Rominger, F.; Metz, M.; Hofmann, P. *Chem. Eur. J.* **1999**, *5*, 557. (c) Vyboishchikov, S. F.; Bühl, M.; Thiel, W. *Chem. Eur. J.* **2002**, *8*, 3962. (d) Fomine, S.; Martinez Vargas, S.; Tlenkopatchev, M. A. *Organometallics* **2003**, *22*, 93. (e) Bernardi, F.; Bottoni, A.; Miscione, G. P. *Organometallics* **2003**, *22*, 940.

10.1021/om030497w CCC: $25.00
Publication on Web 09/25/2003

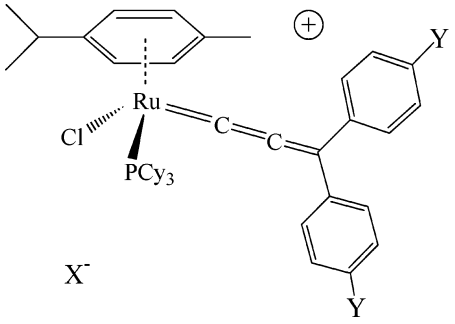
and reaction conditions. Recent kinetic studies have revealed the subtle connection of phosphine dissociation from the precatalyst complex, the initiation step, and the overall catalytic activity.[8]

In the search for alternative metathesis catalysts of comparable performances and improved accessibility, the cationic 18-electron allenylidene ruthenium complexes of formula $[(\eta^6\text{-arene})(PR_3)RuCl(=C=C=CAr_2)]X$ have been shown to be active catalysts in the ring-closing metathesis reaction of α,ω-diolefins and provide an unprecedented example for the involvement of allenylidenes in catalysis.[9] Various synthetic applications in olefin metathesis have been reported that are based on these complexes as precatalysts.[10] The neutral 16-electron allenylidene complex $[RuCl_2(PCy_3)_2(=C=C=CPh_2)]$ and the N-heterocyclic carbene derivative $[RuCl_2(PCy_3)(IMes)(=C=C=CPh_2)]$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) have been tested as catalysts in ring-closing metathesis reactions.[11] However, efficient catalytic activity was exhibited only by the Ru(3-phenylindenylid-1-ene) complexes, corresponding to the formal intramolecular rearrangement of the allenylidene ligand.[12]

The scope of allenylidene complexes in catalysis is rapidly expanding. The aqueous environment is compatible with the activity of allenylidene complexes, since water-soluble complexes of ruthenium(II) perform ring-opening metathesis in water.[13] Cationic cyclopentadienyl ruthenium complexes catalyze the dehydrogenative dimerization of tin hydrides,[14] and ruthenium allenylidene species are intermediates in propargylic substitution reactions.[15]

Since this class of compounds has appeared only recently on the stage of catalysis, scarce is the information about their mode of action as well as the generation and nature of the catalytic species. Extensive work carried out on the ring-closing metathesis reactions of different olefinic substrates, in the presence of various ruthenium allenylidene complexes, $[(\eta^6\text{-arene})(PR_3)RuCl(=C=C=CAr_2)]X$, has given many insights into the process and has left open questions.[9] The ligated phosphine PR_3 affects strongly the performance of the complexes, which decreases in the order $PCy_3 > PiPr_3 \gg PPh_3$. A remarkable effect on the reactivity and selectivity is exerted by the counterion. In fact, the best performance is given by the triflate complex, with respect to the PF_6, BPh_4, BF_4, and $B(C_6F_5)$ analogues, and allows the cyclization of *N*,*N*-diallyltosylamide to proceed at room temperature.[16] The *p*-substituents in the phenyl groups of the allenylidene ligand also affect the product distribution of the reaction. The fact that increased reaction rates of ring-closing metathesis have been obtained upon irradiation of a toluene solution of $[(\eta^6\text{-}p\text{-cymene})(PCy_3)RuCl(=C=C=CPh_2)]PF_6$[10a] has been taken as evidence that a light-induced decomplexation of *p*-cymene liberates a catalytically active 12-electron Ru(II) precursor. This was also observed on irradiation of $RuCl_2(L)(arene)$ complexes[17] and in visible-light-induced ring-opening metathesis polymerization of cyclooctene catalyzed by complexes $[(\eta^6\text{-}p\text{-cymene})RuCl_2(NHC)]$.[2f] The mode of action of the ruthenium precatalysts still appears quite complex.

Using complexes $[(\eta^6\text{-}p\text{-cymene})(PCy_3)RuCl(=C=C=CPh_2)]X$ (X = OTf (CF_3SO_3, **1**), PF_6, BF_4, SbF_6) and $[(\eta^6\text{-}p\text{-cymene})(PCy_3)RuCl(=C=C=C(p\text{-Y-}C_6H_4)_2)]OTf$ (Y = MeO, Cl, F) as precatalysts, rates measurements and spectroscopic studies have been performed on the ring-closing metathesis reaction of *N*,*N*-diallyltosylamide (**2**), chosen as model substrate, and highlight some mechanistic features in the catalytic activity of these allenylidene complexes.



Results and Discussion

Ring-Closing Metathesis Reaction. The ring-closing metathesis reaction of *N*,*N*-diallyltosylamide in the presence of complex $[(\eta^6\text{-}p\text{-cymene})(PCy_3)RuCl(=C=C=CPh_2)]OTf$ (**1**) proceeds smoothly to give the five-membered ring of *N*-tosyl-2,5-dihydropyrrole (**3**), in benzene-d_6. When the reaction is followed in situ by ^1H NMR spectroscopy, the spectra show the disapperance of the $N(CH_2)_2$ signal of the substrate (δ 3.75 ppm, d, J = 6.2 Hz), the formation of the corresponding singlet peak of the product (δ 3.95 ppm), and the appearance of the peak of ethylene (5.29 ppm), as in the expected stoichiometry of the ring-closing metathesis process. The

(8) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.

(9) (a) Fürstner, A.; Liebl, M.; Lehmann, C. W.; Picquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem. Eur. J.* **2000**, *6*, 1847. (b) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315.

(10) (a) Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 2249. (b) Osipov, S. N.; Artyushin, O. I.; Kolomiets, A. F.; Bruneau, C.; Dixneuf, P. H. *Synlett* **2000**, 1031. (c) Osipov, S. N.; Artyushin, O. I.; Kolomiets, A. F.; Bruneau, C., Picquet, M.; Dixneuf, P. H. *Eur. J. Org. Chem.* **2001**, 3891. (d) Sémeril, D.; Olivier-Bourbigou, H.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **2002**, 146. (e) Sémeril, D.; Le Nôtre, J.; Bruneau, C.; Dixneuf, P. H.; Kolomiets, A. F.; Osipov, S. N. *New J. Chem.* **2001**, 16. (f) Castarlenas, R.; Sémeril, D.; Noels, A. F.; Demonceau A.; Dixneuf P. H. *J. Organomet. Chem.*, **2002**, *663* 235. (g) Csihony, S.; Fischmeister, C.; Bruneau, C.; Horvath, I. T.; Dixneuf, P. H. *New J. Chem.* **2002**, 1667.

(11) (a) Schanz, H.-J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187.

(12) (a) Fürstner, A.; Hill, A. F.; Liebl, M.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1999**, 601. (b) Jafarpour, L.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5416. (c) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204. (d) Fürstner, A.; Guth, O.; Düffels, A.; Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811. (e) Harlow, K. J.; Hill, A. F.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1999**, 285.

(13) Saoud, M.; Romerosa, A.; Peruzzini, M. *Organometallics* **2000**, *19*, 4005.

(14) Maddock, S. M.; Finn, M. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2138.

(15) (a) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2003**, *22*, 873. (b) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 11846. (c) Nishibayashi, Y.; Wakiji, I.; Yshii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3393. (d) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019.

(16) Picquet, M.; Touchard, D.; Bruneau, C.; Dixneuf, P. H. *New J. Chem.* **1999**, *23*, 141.

(17) (a) Hafner, A.; Mühlebach, A.; van der Schaaf, P. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2121. (b) Fürstner, A.; Ackermann, L. *Chem. Commun.* **1999**, 95.

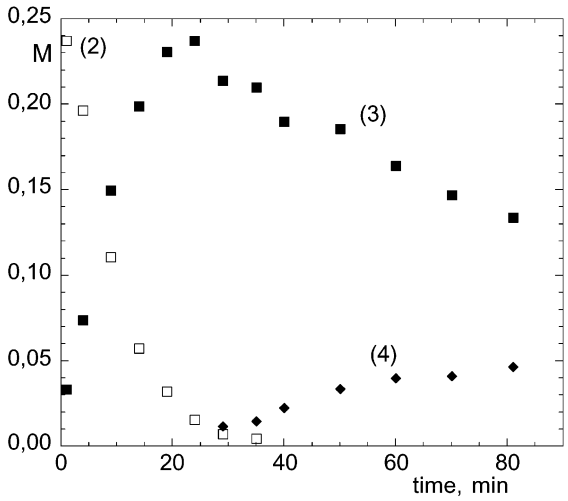
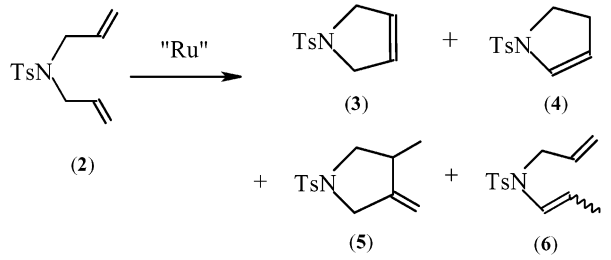


Figure 1. Reaction profile for the ring-closing metathesis of *N*,*N*-diallyltosylamide (**2**, 0.250 M) catalyzed by complex [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]OTf (**1**, 0.017 M, 7 mol %), showing the evolution of the substrate **2** and of products *N*-tosyl-2,5-dihydropyrrole (**3**) and *N*-tosyl-2,3-dihydropyrrole (**4**), in benzene-d_6 at 51.5 °C.

Scheme 1. Overall Product Analysis for the Reactions Catalyzed by Complexes [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CAr_2)]X



experiment carried out using 135 μmol (0.250 M) of substrate and 9.4 μmol of the ruthenium complex (0.017 M, 7 mol %), in the presence of 1,3,5-trimethylbenzene as internal standard, in 500 μL of benzene-d_6 at 51.5 °C, is shown graphically in Figure 1. Most of the experiments have been performed using 0.250 M of *N*,*N*-diallyltosyl amide and 7 mol % of complex **1**, at 51.5 °C, unless indicated otherwise.

The plot shows a conversion of substrate into the product of ring-closure larger that 90% within 20 min of reaction. A slower transformation of **3** into the *N*-tosyl-2,3-dihydropyrrole (**4**) isomer occurs afterward (Scheme 1). Such olefin isomerization has been observed sporadically in the case of ring-closing metathesis reactions catalyzed by the first- and second-generation Grubb's catalysts and has been recently optimized by introduction of additives to perform tandem ring-closing metathesis−olefin isomerization[18] or tandem alkene isomerization−Claisen rearrangement reactions.[19]

The performance of analogues of complex **1** containing counterions different from triflate, namely, the complexes [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]X (X = PF_6, BF_4, SbF_6), was investigated under identical conditions used for **1**. The reaction catalyzed by the PF_6 derivative, although quite slow (~3 h for half consumption of the initial amount of **2**), proceeds selectively to form the cyclic compound **3**, without traces of byproducts from olefin isomerization. On the other hand, the catalysis by the BF_4 complex is more rapid ($[\mathbf{2}]_0$ reduces by half in ~30 min) but displays scarce selectivity: the formation of **3** is accompanied by large quantities of the methylenecyclopentane derivative **5** and of an isomer of the substrate, in which one allylic double bond has rearranged to the 1-position (**6**).[9a] The various possible products resulting from *N*,*N*-diallyltosylamide are shown in Scheme 1. Relatively slow is also the reaction catalyzed by the SbF_6 complex, with formation of small quantities of **6** (about 10% with respect to **3**), and further isomerization of **3**.

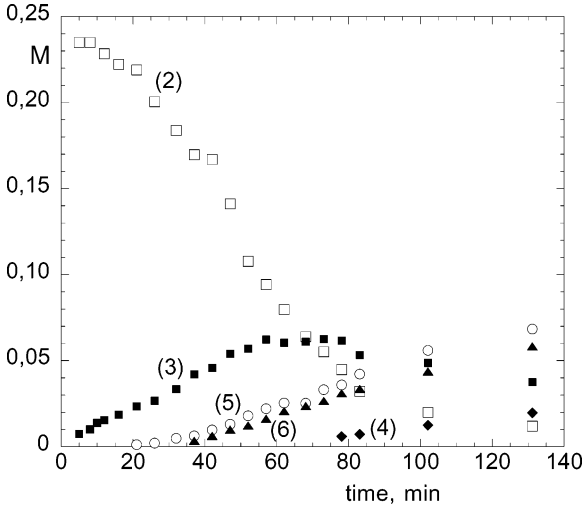


Figure 2. Reaction profile for the ring-closing metathesis of *N*,*N*-diallyltosylamide (0.250 M) catalyzed by complex [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=C(*p*-MeO-C_6H_4)$_2$)]OTf (0.017 M, 7 mol %), in benzene-d_6 at 51.5 °C, showing the evolution of the substrate **2** and of products **3**, **4**, **5**, and **6**.

The effect of the *p*-substituent of the allenylidene aryl rings has been investigated by performing the reaction in the presence of complexes [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=C(*p*-Y-C_6H_4)$_2$)]OTf (Y = MeO, Cl, F), in benzene-d_6 at 51.5 °C. The consumption of the substrate is twice as fast with the *p*-Cl and *p*-F derivatives than with the *p*-methoxy complex, while the selectivity is poor in all cases. Figure 2 shows a reaction profile in the case of complex [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=C(*p*-OMe-C_6H_4)$_2$)]OTf. The plot shows the presence of a consistent induction time period, indicating slow conversion of the precatalyst into the catalytically active species. As in most cases, the products **5** and **6** appear after about 20 min of reaction, implying that their formation is due to species resulting from degradation of the metathesis catalyst.

The fact that the metathesis reactions catalyzed by complex **1** or by the PF_6 derivative proceed smoothly and selectively just above room temperature indicates that the active catalytic species is obtained in a process of thermal activation. This is comparable with the photochemical activation by irradiation with UV light, performed at lower temperature. For instance, *N*,*N*-diallyltosylamide was converted into the cyclic product (81%) under irradiation at 300 nm for 5 h in the

(18) Sutton, A. E.; Seigal, B. A.; Finnegan, D. F.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 13390, and references therein. (b) Alcaide, B.; Almendros, P. *Chem. Eur. J.* **2003**, *9*, 1259.

(19) (a) Le Nôtre, J.; Brissieux, L.; Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **2002**, 1772. (b) Ben Ammar, H.; Le Nôtre, J.; Salem, M.; Kaddachi, M. T.; Dixneuf, P. H. *J. Organomet. Chem.* **2002**, *662*, 63.

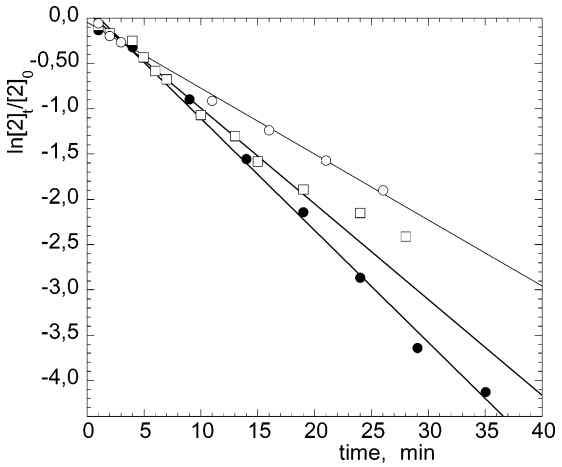


Figure 3. Logarithmic plots ($\ln[\mathbf{2}]_t/[\mathbf{2}]_0$) vs time) for the ring-closing metathesis of *N*,*N*-diallyltosylamide (**2**, 0.250 M) catalyzed by complex [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]OTf (**1**, 0.017 M, 7 mol %), in benzene-d_6 at 51.5 °C. The runs have been performed immediately after mixing (●) or after preheating the solution of complex **1** for 10 (□) or 30 min (○).

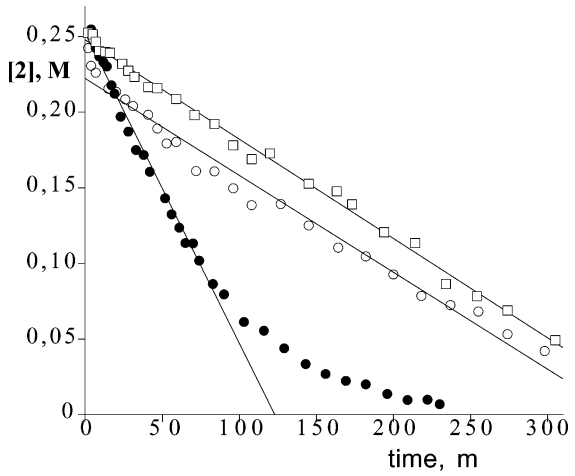


Figure 4. Evolution of *N*,*N*-diallyltosylamide (**2**, 0.29 M) vs time, for the ring-closing metathesis catalyzed by complex **1** (5 mol %) in benzene-d_6 (●), in dichloromethane-d_2 (○), and in dichloromethane-d_2 in the presence of added *p*-cymene (0.54 M) (□), at 33 °C.

presence of complex [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]PF_6 (2.5 mol %) in toluene at 20 °C.[9a] The same PF_6 complex (7 mol %) catalyzes the formation of **3** with 75% of conversion after 9 h at 51.5 °C.

A plot of $\ln([\mathbf{2}]_t/[\mathbf{2}]_0)$ versus time for the reaction shown in Figure 1 is linear (Figure 3, ●) and allows obtaining a value of the observed rate constant based on the disapperance of the diene, which is $k_{obs} = 2.06 \times 10^{-3}$ s^{-1}. A first-order dependence of the reaction on the diene may occur if eq 1 applies to the system

$$-\frac{d[\mathbf{2}]}{dt} = k_c[\mathbf{2}][\text{catalyst}]^y = k_{obs}[\mathbf{2}] \qquad (1)$$

in which $k_{obs} = k_c[\text{catalyst}]^y$, and k_c is the rate constant of the catalytic reaction. If the catalyst concentration, [catalyst], is constant, since it refers to a species regenerated essentially as fast as it is consumed, then pseudo-first-order conditions are ensured.[20] Although the overall process is rather complex, comprising (i) activation of the precatalyst, (ii) initiation step, and (iii) propagation (vide infra), the first-order fit obtained upon following the disappearance of **2** suggests that steps i and ii are faster than the actual metathesis reaction. The linear dependence observed for more than 95% of substrate conversion ($\sim 4\tau_{1/2}$) indicates that the catalytic species, once formed, maintains a constant concentration until most of the substrate is consumed, and degradation occurs only toward the end of the metathesis process. Experiments obtained using different amounts of the triflate complex between 0.012 (5 mol %) and 0.032 (13 mol %) M exhibit clearly a rate dependence on [**1**]. However, the accessible range of concentration is too small in order to allow a clean definition of the reaction order on **1** and therefore to define the *y* exponent in eq 1. Complex kinetics are exhibited in the cyclization reaction of diethyl diallylmalonate catalyzed by the alkylidene complexes [$RuCl_2$-(PCy_3)$_2$(=CHR)] (R = Ph, CH=CHPh), in dichloromethane-d_2. In the case of the methylidene species [$RuCl_2$-(PCy_3)$_2$(=CH_2)], first-order behavior was obtained in the presence of excess PCy_3.[4a]

The active catalytic species in solution undergoes thermal degradation in the absence of the olefin substrate. In fact, when benzene-d_6 solutions of complex **1** in the NMR tube are maintained at 51.5 °C for 10 or 30 min before addition of **2**, the subsequent reactions proceed at decreasing rates, being $k_{obs} = 1.8 \times 10^{-3}$ (10 min) and 1.2×10^{-3} s^{-1} (30 min), respectively (Figure 3). In addition, the logarithmic plots deviate consistenly from linearity after about 80% of reaction.

A first-order behavior is maintained at higher temperatures in benzene-d_6 (e.g., 64 °C, $k_{obs} = 7.6 \times 10^{-3}$ s^{-1}). When experiments are performed at lower temperatures (e.g., 35 and 42 °C), nearly quantitative conversions of **2** are obtained at longer reaction times, indicating generation and activity of the catalyst under modest thermal activation. The catalytic activity appears solvent dependent. The reaction catalyzed by **1** (0.0147 M, 5 mol %) proceeds in a similar vein in both benzene-d_6 and dichloromethane-d_2 at 33 °C, but slower conversion of the substrate (0.297 M) is observed in the latter solvent (Figure 4). Higher activity was found for reactions catalyzed by [$RuCl_2$(PCy_3)(=CHPh)(IMes)] in toluene than in dichloromethane.[12c] In contrast, ring-closing metathesis of diethyl diallylmalonate catalyzed by [$RuCl_2$(PCy_3)$_2$(=CHR)] complexes was found to be 3 times faster in dichloromethane than in benzene.[4a]

One significant feature of the experiments performed just above room temperature (33 °C) is that the change of [**2**] versus time is not exponential any more but rather linear, indicating a reaction that is zero-order in the olefinic substrate (Figure 4).[21] This evidence suggests that transformation of complex **1** into a catalytically key

(20) Hammett L. P., *Physical Organic Chemistry*; McGraw-Hill: New York, 1970; p 55.

(21) The zero-order plots are linear up to about 80% of reaction. The deviation from linearity observed for the reaction in benzene-d_6 after 90 min, at about 70% of conversion (Figure 4), may be ascribed to the overriding presence of inorganic decomposition products with respect to complex **1** and to the catalytic species after this reaction time. The clear-cut difference between first-order and zero-order dependence on the substrate is striking upon comparing the plots of [**2**] vs time of the experiments performed at 64 and 35 °C, respectively, in benzene-d_6 (7 mol % of **1**).

species has become significantly slower, and therefore rate determining, with respect to the metathesis process. The ring-closing reaction occurs as soon as this species is available, resulting in zero-order dependence on **2**. Such a drastic change in rate-determining step with temperature may be interpreted in terms of the different molecularities of the activation, initiation, and propagation stages. The activation (i) of the precatalyst corresponds to a chemical transformation of complex **1** into a reactive species (**1***) (eq 2), which enables interaction with the olefinic substrate to produce the effective catalytic species, "catalyst" of eq 1, presumably a ruthenium carbene, in the initiation step (ii). The actual ring-closing metathesis reaction is carried out by the catalyst in the propagation stage (iii). According to this picture, the unimolecular activation of **1** should exhibit a larger effect by changes in temperature than the initiation and propagation steps, characterized by bimolecular interactions between catalytic active species and the substrate.[22] In the lower temperature range, the reaction rate would therefore be represented by eq 3.

step i: Complex **1** → **1*** (2)

$$-\frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = k_0 \qquad (3)$$

The activation process is faster in benzene-d_6 than in dichloromethane-d_2. The slopes of the lines in Figure 4 represent the rate constants which are zero-order in **2**, with values of $k_0 = 3.4 \times 10^{-5}$ M s^{-1} in benzene-d_6, $k_0 = 1.06 \times 10^{-5}$ M s^{-1} in dichloromethane-d_2 ([**1**] = 0.0147 M), and $k_0 = 1.10 \times 10^{-5}$ M s^{-1} in dichloromethane-d_2 containing added *p*-cymene (0.54 M) at a lower content of complex **1** (0.0132 M). These reactions in dichloromethane-d_2 exhibit about 97% selectivity, evaluated in the range of 80−90% conversion of the olefin (≅5 h of reaction). A change from zero-order dependence on substrate to first-order dependence has been reported for the polymerization of norbornene catalyzed by complex [(η^6-*p*-cymene)(PCy_3)$RuCl_2$], in the absence or presence of (trimethylsilyl)diazomethane as catalyst initiator.[23]

It is a common feature in catalysis that the access to the active metal species occurs by ligand dissociation especially from an 18-electron precatalyst metal complex. This process liberates open coordination site(s) for interaction with the substrate. Phosphine dissociation from the 16-electron complexes [$RuCl_2(PCy_3)_2$(=CHR)], as well as from the related N-heterocyclic carbene derivatives, has been proved and described in detail from rate studies, carried out by kinetic measurements and ^{31}P NMR magnetization transfer experiments.[8] It has been shown that exchange of phosphine by olefin occurs via a dissociative mechanism which yields the 14-electron intermediate [$RuCl_2(PCy_3)$(=CHPh)]. Since the cationic allenylidene complexes [(η^6-*p*-cymene)(PR_3)-RuCl(=C=C=CAr_2)]X are saturated 18-electron species, the occurrence of ligand dissociation as one of the first stages toward activation is most likely. Decoordination of *p*-cymene to yield a highly reactive 12-electron complex and/or phosphine dissociation to give a 16-electron complex have been proposed.[16] A basic experiment in order to probe the existence and influence of a ligand dissociative step consists of the addition of free ligand to the reaction mixture, with an expected rate decrease when an equilibrium between free and bound ligand is involved, as in the case of complex [$RuCl_2$-(PCy_3)$_2$(=CH_2)].[4a] The presence of an excess of PCy_3 (0.15 M, 51.5 °C) in the reaction of *N*,*N*-diallyltosylamide and complex **1** caused both slow consumption of substrate and a change of reaction destiny. In fact, only traces of the ring-closing metathesis product **3** were detected, while the main product was the substrate isomer **6.** The experiment is shown graphically in Figure 5. This compound had already been found as a byproduct present in relevant amounts in the reactions catalyzed by the BF_4 and $B(C_6F_5)_4$ analogues of complex **1**, as a result of the different counteranion of the precatalyst.[9a] Competing metathesis condensation reactions and olefin isomerization of allylic compounds in the presence of ruthenium catalysts have been reported.[24] The presence of less than 0.15 M of PCy_3 caused the formation of both the ring-closing and the isomerization product. Visually, the addition of PCy_3 to a solution of **2** and of complex **1** changes the color from red to orange-yellow, the same color change observed upon degradation of the catalytic species at the end of the reactions. This indicates that the presence of excess phosphine changes drastically both the nature of the allenylidene complex and the catalytic properties. This approach, which proved to be a valid resort in the case of [$RuCl_2$-(PCy_3)$_2$(=CH_2)],[4a] cannot be used for further kinetic elaboration about the formation of the active species from complex **1**. This diversity as well as the solvent effect here observed suggest the existence of different catalytic species in the reactions catalyzed by complex **1** and by the Grubb's catalysts.

Addition of excess *p*-cymene to the reaction mixtures in benzene-d_6 at 52 °C had no appreciable effects on the

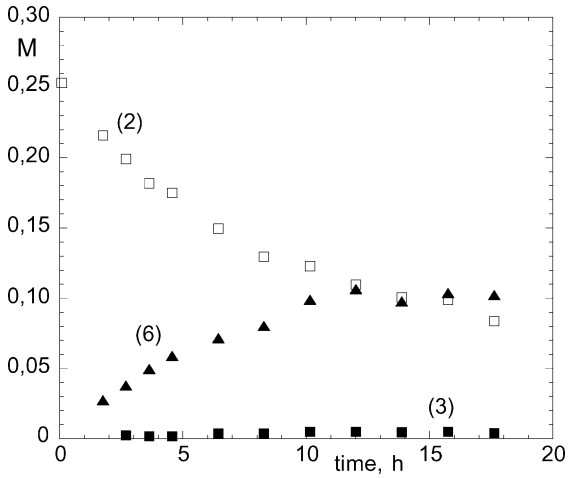


Figure 5. Evolution of *N*,*N*-diallyltosylamide (**2**, 0.250 M) and of products **3** and **6** for the reaction in the presence of complex [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]OTf (**1**, 0.017 M, 7 mol %) and of PCy_3 (0.15 M), in benzene-d_6 at 51.5 °C.

(22) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: New York, 1985; p 253.

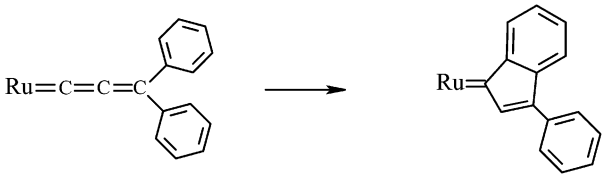
(23) Demonceau, A.; Stumpf, A. W.; Saive, E.; Noels, A. F. *Macromolecules* **1997**, *30*, 3127.

(24) (a) Sworen, J. C.; Pawlow, J. H.; Case, W.; Lever, J.; Wagener, K. B. *J. Mol. Catal. A: Chem.* **2003**, *194*, 69. (b) Lehman, S. E.; Schwendeman, J. E.; O'Donnell, P. M.; Wagener, K. B. *Inorg. Chim. Acta* **2003**, *345*, 190.

reaction rates. To avoid ambiguities arising from structural affinities between the ligand and the solvent, and therefore effects from exchange phenomena of the arenes, the influence of added *p*-cymene was evaluated in experiments in dichloromethane-d_2. The case shown in Figure 4 (33 °C) in which neither reactivity nor selectivity is affected by the presence of free arene seems to indicate that release of *p*-cymene from complex **1** does not play a role in the activation of the precatalyst, at least at these temperatures. However, it is possible that decoordination of *p*-cymene occurs after the rate-limiting step or that the other ligands reorganize themselves around the metal after release of the arene, thus disfavoring reversible coordination. Such a process may become more significant at higher temperatures. In fact, it has been reported previously that the yield of product **3** was reduced by more than half upon addition of *p*-cymene in the reaction catalyzed by complex [(*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]PF_6, in toluene at 80 °C.[9a] The absence of the arene group in the propagating carbene ruthenium complex for the polymerization of cyclooctene or norbornene catalyzed by the system [(η^6-*p*-arene)$RuCl_2$]/PCy_3/Me_3SiCHN_2 was shown by ^{1}H NMR studies, although some features of the polymer were actually affected by the nature of the arene (benzene, *p*-cymene, hexamethylbenzene) in the starting ruthenium complex.[23]

Spectroscopic Analysis and Solution Properties of Complex [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]OTf. The Activation Stage. The solution properties and thermal stability of complex **1** have been investigated by ^{1}H, ^{31}P NMR, FT-IR, and UV−visible spectroscopy. In a solution of **1** in benzene-d_6, the four doublets of coordinated *p*-cymene, found at δ 6.52, 6.45, 6.28, and 5.97 (J = 6.5 Hz) at room temperature, decrease in intensity at 41 °C and disappear completely within half an hour. This is accompanied by disappearance of the allenylidene peaks (δ 7.77, d; 7.26, t; 7.08, t) in the aromatic region and by the presence of new peaks at 7.95, 7.67, 7.59 (d), 7.3−7.2 (m), 7.03, 7.02, 5.35 (s) ppm, while free *p*-cymene is observed in the aliphatic region. The room-temperature ^{31}P NMR spectrum of **1** in benzene-d_6 shows the peak of coordinated PCy_3 at δ 60.2 ppm. After about 20 min at 40 °C, new peaks have appeared at δ 55.1, 52.1, 30.3, 29.5, and 27.7 ppm. At 52 °C, the peak of the starting material and dominant peaks are found at δ 52.3, 30.3, and 29.5 ppm. When a similar experiment was carried out in the presence of *N*,*N*-diallyltosylamide, the main peaks are observed at δ 60.4, 29.5, and 27.6 ppm (52 °C). When a solution of **1** in dichloromethane-d_2 is heated and various ^{1}H NMR spectra are monitored up to 40 °C, no significant changes are observed. The addition of different aliquots (5, 10, 20 μL) of benzene-d_6 causes a rapid decrease of the aromatic peaks of coordinated *p*-cymene and extensive formation of the free ligand, which suggests an exchange reaction between the arene molecules.[25] On the other hand, the peaks of the allenylidene moiety are still clearly visible. The ^{31}P NMR spectra in dichloromethane-d_2 indicate only minor decomposition of complex **1** (60.1 ppm) upon warming, shown by the appearance of very small peaks at δ 58.3, 37.4, 31.8, 30.8, 29.1, and 28.4 ppm. These NMR analyses indicate that the transformation of complex **1** in solution is rather complex. The situation appears simplified in the presence of the substrate **2**, in which case the active species is (are) probably swept by the olefin to enter the catalytic cycle. The larger thermal stability of complex **1** observed in dichloromethane-d_2 than in benzene-d_6, in particular that of the allenylidene group, parallels the higher catalytic activity observed in the latter solvent and suggests that the activation of the complex toward the catalytic species involves essentially the allenylidene moiety.

Scheme 2. Intramolecular Transformation of the Ruthenium-Allenylidene Fragment of Complex 1 into a Ruthenium-Indenylidene Moiety



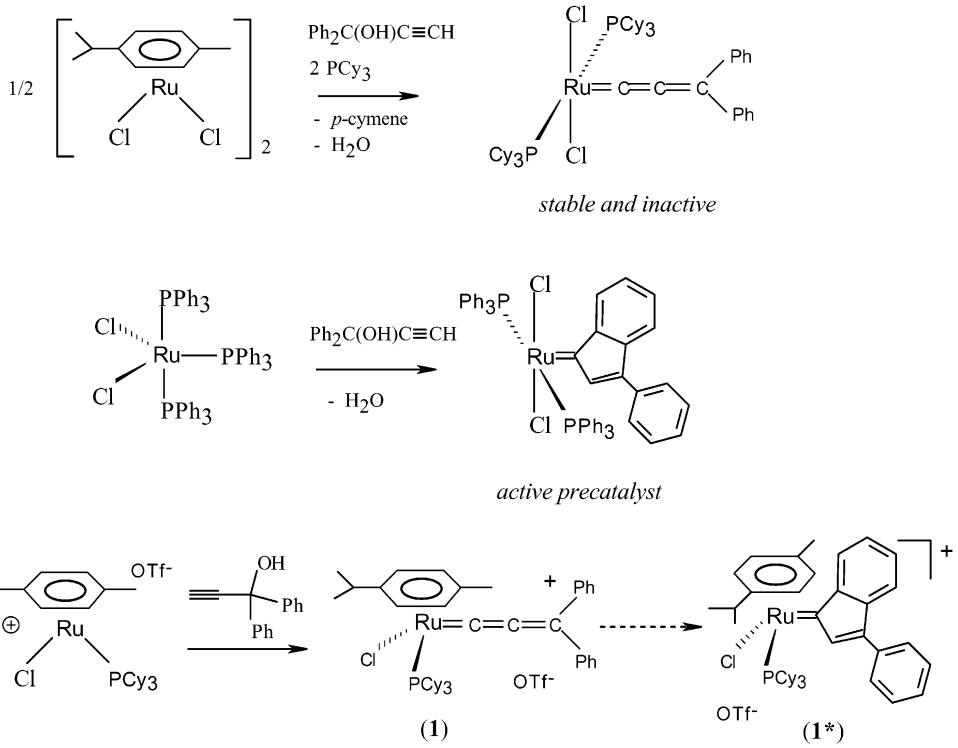
The FT-IR spectrum of **1** is characterized by an intense band at 1963 cm^{-1} in $CDCl_3$, due to the stretching vibration of the allenylidene group. The band is broader in benzene-d_6, with a maximum at 1955 cm^{-1} and a high-frequency shoulder, probably due to the presence of conformers in solution. Upon warming a solution of **1** in benzene-d_6 (52 °C), the allenylidene band decreases rapidly until complete disappearance (<10 min), both in the absence and in the presence of the olefin **2**. Small residual absorptions are observed in the same frequency range (1962−1955 cm^{-1}) at the end of the catalytic cycle, indicating the presence of species different from the parent complex. These experiments confirm the involvement of the allenylidene band in the thermal transformation of complex **1** and the unimolecular nature of the activation stage, which was inferred from the experiments of catalysis.

Although a definitive description of the chemical fate of complex **1** in the direction of catalysis, i.e., in the formation of the effective catalytic species, is still out of reach, the most likely hypothesis involves a thermally promoted intramolecular rearrangement of the C=C=CPh_2 group into a 3-phenylindenylidene ligand (Scheme 2). It has been proposed that such a process may be triggered by reduced electron density on ruthenium.[11] In this case, temporary release of phosphine, decoordination of *p*-cymene, arene exchange, or their combinations may affect the rate of this transformation. More detailed quantitative studies are needed in order to assess more properly the influence of these processes.

The occurrence of an allenylidene−phenylindenylidene rearrangement is supported by UV−visible spectra of complex **1** in toluene at 50 °C, which show a rapid decrease of the strongest band in the visible region at 518 nm, essentially due to the allenylidene group, as well as of the smaller band at 358 nm, and the simultaneous appearance of a new absorption at 409 nm, consistent with the formation of a new metal unsaturated moiety. The occurrence of such a rear-

(25) However, attempts to perform the exchange of *p*-cymene with benzene under preparative conditions have resulted only in the formation of decomposition products. The occurrence of "intramolecular" arene exchange has been reported recently: Çetinkaya, B.; Demir, S.; Özdemir, I.; Toupet, L.; Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Chem. Eur. J.* **2003**, *9*, 2323.

Scheme 3. Structural and Activity Features of Allenylidene and Indenylidene Complexes



rangement is in line with the observations reported in the literature, in particular with the relation between stability of the ruthenium-allenylidene moiety and catalytic activity. In fact, the allenylidene complexes $[RuCl_2(=C=C=CPh_2)(PCy_3)_2]$ and $[RuCl_2(=C=C=CPh_2)(PCy_3)(IMes)]$, which are thermally stable (80 °C in toluene-d_8, 32 h), perform poorly as ring-closing metathesis catalysts.[11] On the other hand, complexes of type $[RuCl_2(PR_3)_2(3\text{-phenylindenylid-1-ene})]$ and $[RuCl_2(PR_3)(IMes)(3\text{-phenylindenylid-1-ene})]$ (R = Ph, Cy) were found to be efficient alkene metathesis catalyst precursors.[12] It is interesting to note that the reaction of $Ph_2C(OH)C{\equiv}CH$ with the neutral complex $[RuCl_2(PPh_3)_3]$ yields an indenylidene species, $[RuCl_2(PPh_3)_2(3\text{-phenylindenylid-1-ene})]$,[11,12d] and not the expected allenylidene complex,[12e] while the same reaction with the cationic compounds $[(\eta^6\text{-}p\text{-cymene})(PCy_3)RuCl]X$ produce relatively stable allenylidene complexes.[9] The direct intramolecular allenylidene−indenylidene transformation from the reaction between a ruthenium precursor and propargylic alcohol has never been observed.[12d] These considerations are represented in Scheme 3. As a blank experiment, a benzene-d_6 solution of $[(\eta^6\text{-}p\text{-cymene})(PCy_3)RuCl]OTf$ does not display any catalytic activity, while a solution of the same complex (7 mol %) with an equimolar amount of $Ph_2C(OH)C{\equiv}CH$ exhibits a clean and selective transformation of the bis-allyl compound **2** into the product of ring-closing metathesis, due to formation in situ of complex **1**, as an additional proof of the key role played by the allenylidene moiety. In this case, a plot of [**2**] and [**3**] versus time shows a typical induction period in the early stage of the process, since an additional reaction now precedes the formation of the catalytic species. The process most similar to the allenylidene−indenylidene rearrangement here proposed is the intramolecular transformation of a pentatetraenylidene ruthenium complex into an indenylallenylidene compound, which occurs in chloroform at room temperature via an electrophilic aromatic substitution process.[26]

It is noteworthy that the ruthenium-indenylidene complex **1*** has recently been obtained and characterized by NMR at low temperature.[27] However, in that case it arises from protonation of **1** at low temperature (−40 °C) with the strong acid TfOH, giving first the corresponding alkenylcarbyne-ruthenium species that rearranged into the indenylidene-ruthenium species **1*** at −20 °C. Thus, it is very likely that the thermal transformation of allenylidene **1** also affords the same species **1***. It is also likely that steric interaction of the indenylidene and *p*-cymene ligands in **1*** favors the decoordination of the *p*-cymene group to give the active species.

Other parallel transformations may account for the disappearance of the allenylidene band of complex **1** as well as the formation of active catalytic species and may explain the complexity observed in the ^{31}P NMR spectra. For instance, it is known that neutral allenylidene species are characterized by an infrared absorption of lower intensity than that of the corresponding cationic complexes.[12e] Recently, an intramolecular migration of phosphine onto the α-carbon atom of the allenylidene group has been reported, following the reaction of complex $[(\eta^6\text{-}C_6Me_6)RuCl_2(PPh_2CH{=}CH_2)]$ with $Ph_2C(OH)C{\equiv}CH$,[28] and the occurrence of an analogous coupling in our system cannot be excluded.

(26) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157.
(27) Castarlenas, R.; Dixneuf, P. H. *Angew. Chem., Int. Ed.*, accepted for publication.
(28) Hansen, H. D.; Nelson, J. H. *Organometallics* **2000**, 19, 4740.

Conclusions

^{1}H NMR in situ experiments for the ring-closing metathesis reaction of *N*,*N*-diallyltosyl amide catalyzed by [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2)]OTf and related complexes represent a convenient method to monitor the reaction progress as well as to compare selectivity and efficiency of the process under different conditions and reaction times. Best selectivities are exhibited by the triflate and by the hexafluorophosphate complexes, under thermal activation, the latter performing a slower reaction. The addition of free phosphine in the reaction mixture inhibits the metathesis reaction, implying that lability of PCy_3 is important for the catalytic activity, and activates a slower isomerization process of the diolefin. The reactions catalyzed by complex **1** exhibit a first-order dependence on the olefinic substrate above 50 °C, due to rate-determining ring-closing metathesis, while a zero-order dependence on *N*,*N*-diallyltosylamide is observed at lower temperatures, since the activation of complex **1** becomes the slowest step. Faster reactions in benzene-d_6 than in dichloromethane-d_2 and lack of rate depression in the presence of added *p*-cymene are observed. Spectroscopic experiments carried out on solutions of complex **1** confirm faster transformation of complex **1** in benzene-d_6 than in dichloromethane-d_2 and indicate that the chemical transformation of the precatalyst regards essentially the allenylidene group. Both rate and spectroscopic studies support the thermal intramolecular rearrangement of the allenylidene into an indenylidene ligand, before or after release of the arene ligand to generate a coordinatively unsaturated catalytic species.

Experimental Section

General Procedures. ^{1}H NMR: Bruker AM 200 or AC 300 P. Chemical shifts are reported in δ values relative to tetramethylsilane; $CHCl_3$ ($\delta = 7.25$), CH_2Cl_2 ($\delta = 5.32$), and C_6H_6 ($\delta = 7.15$) were used as internal standards. Dichloromethane for the synthesis of the precatalyst complexes was dried and distilled over CaH_2. Compounds **2** and **3**,[29] **4**,[30] **5**,[31] and **6**[9a] have been previoulsy reported and were identified on the basis of the corresponding peaks in the ^{1}H NMR spectra and by GC/MS analyses. FT-IR: Nicolet 510 (Software Omnic 4.1a) in 0.1 or 0.5 mm CaF_2 solution cells fitted with a thermostated jacket. UV−vis spectra: Perkin-Elmer Lambda 18.

Ring-Closing Metathesis Experiments and Kinetic Measurements. All manipulations were performed under argon and Schlenk line techniques. The precatalyst complex was prepared by reacting in a tube equimolar amounts of propargylic alcohol $Ar_2C(OH)C{\equiv}CH$ and [(η^6-*p*-cymene)(PCy_3)-RuCl]X for 20 min in dichloromethane at room temperature. The solvent was removed under vacuum (1 h) to leave the desired [(η^6-*p*-cymene)(PCy_3)RuCl(=C=C=CAr_2)]X complex as a red dark solid. The appropriate amount of complex (e.g., 8.5 mg for 7 mol % of **1** with respect to **2**) was weighed into a 5 mm NMR tube, two vacuum-argon cycles were performed, then the deuterated solvent (500 μL), *N*,*N*-diallyltosylamide (34 mg) and in some cases 1,3,5-trimethylbenzene (9 μL) as internal standard for peak integration were added by microsyringe and the tube was sealed with a rubber cap. The tube was shaken just before introduction into the NMR probe, and the experiment performed after about 1 min, allowing for thermal equilibration and instrument setup. A macrosequence was used to collect spectra at regular interval times. The temperature in the probe (±0.3 °C) was determined from the chemical shift difference between OH and CH_2 signals of a solution of ethylene glycol containing 20% dimethyl sulfoxide-d_6.[32] Values of observed rate constants (k_{obs}, s^{-1}) for consumption of **2** were obtained by fitting the exponential dependence of concentration, *C*, against time, according to the first-order rate equation (eq 4):

$$C_t = C_\infty + (C_0 - C_\infty)\exp(-k_{obs}t) \qquad (4)$$

The k_{obs} values, which were reproducible within 10%, were checked against those obtained from straight line plots of ln(C/C_0) against time. The correlation coefficients (R) of the linear plots of zero- and first-order reactions were ≥0.99. The concentration values were obtained by peak integration of substrate (−$N(CH_2)_2$) and products with respect to the overall resonances of the tosyl methyl groups (Me-C_6H_4−) to 1,3,5-trimethylbenzene or to free *p*-cymene when added in excess.

Acknowledgment. We thank the program COST CHEMISTRY, Working Group "Ruthenium Catalysts for Fine Chemistry" (D12/0025/99) for a travel grant to D.S.

OM030497W

(29) Cerzo, S.; Cortés, J.; Moreno-Mañas, M.; Pleixats, R.; Roglans, A. *Tetrahedron* **1998**, *54*, 14869.
(30) Kinderman, S. S.; van Maarseveen, J. H.; Schoemaker, H. E.; Hiemstra, H.; Rutjes, F. P. J. T. *Org. Lett.* **2001**, *3*, 2045.
(31) Radetich, B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 8007.
(32) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.