

Room temperature operating allenylidene precatalyst $[\text{L}_n\text{Ru}=\text{C}=\text{C}=\text{CR}_2]^+\text{X}^-$ for olefin metathesis: dramatic influence of the counter anion X^-

Michel Picquet, Daniel Touchard, Christian Bruneau and Pierre H. Dixneuf*

Laboratoire Organométalliques et Catalyse, UMR 6509 CNRS-Université de Rennes, Campus de Beaulieu, F-35042 Rennes, France

Received (in Montpellier, France) 12th November 1998, Accepted 2nd December 1998

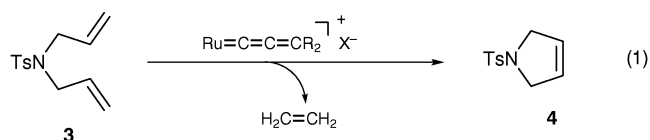
The allenylidene-ruthenium(II) complex $[(p\text{-cymene})(\text{PCy}_3)\text{ClRu}=\text{C}=\text{C}=\text{CPh}_2]^+\text{X}^-$, **2a**, ($\text{X}^- = \text{CF}_3\text{SO}_3^-$), which is produced in a one-pot reaction from commercially available $[\text{RuCl}_2(p\text{-cymene})]_2$, catalyses the ring-closing metathesis of *N,N*-diallyltosylamide **3** at room temperature whereas **2b** ($\text{X}^- = \text{BF}_4^-$) favours the cyclization of the 1,6-diene **3** into the five-membered heterocycle **5** without loss of atoms. The addition of $\text{BF}_3 \cdot \text{OEt}_2$ to **2b** restores its selectivity in the RCM reaction. Catalyst **2a** also promotes the metathesis of the ene-yne **6** to produce the 3-vinyl-2,5-dihydrofuran **7**.

Alkene metathesis has now emerged as a widely applicable methodology for organic synthesis,¹ especially *via* ring-closing metathesis (RCM)² or ring-opening cross-metathesis (ROM),³ including the generation of optically active compounds.⁴ This development was made possible by the discovery of well-defined, soluble molecular catalysts tolerating a variety of functional groups, such as the ruthenium carbene complexes $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHR}$.⁵ The efficiency and advantages of these ruthenium carbene catalysts have motivated the search for more straightforward ways to produce neutral, 16-electron ruthenium complexes containing the secondary $\text{Ru}=\text{CHR}$ moiety and bulky phosphines^{6,7} or carbene ligands.⁸ Recently, it was found that the 18-electron cationic allenylidene complexes of the type $[(\text{arene})(\text{PR}_3)\text{ClRu}=\text{C}=\text{C}=\text{CPh}_2][\text{PF}_6]$,⁹ containing only one bulky phosphine ($\text{PR}_3 = \text{PCy}_3$, PPri_3) per ruthenium site and a non-coordinating anion, constituted a new class of RCM catalysts in the same range of activity (80 °C for several hours) as the 16-electron, neutral $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHR}]$ complexes.⁵ The efficiency of these cationic precatalysts raises, however, the question of the influence of the counter anion.

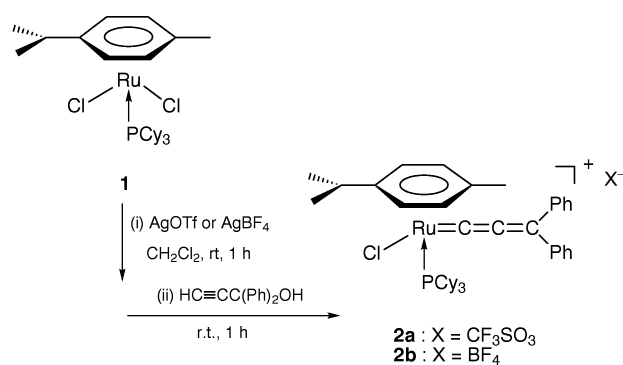
Now we report (i) the first example of an allenylidene precatalyst able to perform the RCM reaction at room temperature, namely the derivative $[(p\text{-cymene})(\text{PCy}_3)\text{ClRu}=\text{C}=\text{C}=\text{CPh}_2][\text{O}_3\text{SCF}_3]$, **2a**, prepared in a one-pot reaction from commercially available $[\text{RuCl}_2(p\text{-cymene})]_2$ and *via* $\text{RuCl}_2(\text{PCy}_3)(p\text{-cymene})$ **1**, (ii) evidence for the unexpected dramatic influence of the counter anion X^- on the catalytic activity of the $[\text{L}_n\text{Ru}=\text{C}=\text{C}=\text{CPh}_2][\text{X}]$ salts, (iii) that the counter anion BF_4^- in precursor **2b** by contrast favours the cyclization of a 1,6-diene with atom economy, (iv) that the addition of the Lewis acid BF_3 restores the activity and selectivity of **2b** as a RCM catalyst and (v) the ability of **2a** to perform the catalytic metathesis of ene-yne into vinyl dihydrofuran.

In order to evaluate whether the counter anion X^- in the catalyst precursors $[(\text{arene})(\text{PR}_3)\text{ClRu}=\text{C}=\text{C}=\text{CPh}_2]^+\text{X}^-$, **2**, had an influence on olefin metathesis, new complexes of type **2** containing the bulky PCy_3 ligand and various X^-

anions have been prepared. Their activity in RCM catalysis was studied in the transformation of the simple *N,N*-diallyltosylamide **3** into the *N*-tosyldihydropyrrole **4** as a model reaction:



The precursors **2a** ($\text{X}^- = \text{CF}_3\text{SO}_3^-$) and **2b** ($\text{X}^- = \text{BF}_4^-$) were obtained by treatment of the complex $\text{RuCl}_2(\text{PCy}_3)(p\text{-cymene})$, **1**, with a slight excess of AgOTf or AgBF_4 in dichloromethane at room temperature to generate *in situ* the isolatable 16-electron intermediate $[(p\text{-cymene})(\text{PCy}_3)\text{ClRu}]^+\text{X}^-$. The addition to the latter of an excess of $\text{HC}\equiv\text{CC}(\text{Ph})_2\text{OH}$ in dichloromethane led to the isolation of fully characterized **2a** and **2b** in 95% yields (Scheme 1).[†] $[(p\text{-cymene})(\text{PCy}_3)\text{ClRu}]^+[\text{BPh}_4]^-$, **2c**, was also obtained in 95% yield by reaction of **1** with an excess of NaBPh_4 in methanol in the presence of 1.5 equiv. of $\text{HC}\equiv\text{CC}(\text{Ph})_2\text{OH}$.[†]



Scheme 1

The transformation of **3** (0.5 mmol) into **4** was performed with 2.5 mol% of isolated $[\text{Ru}=\text{C}=\text{C}=\text{CPh}_2]^+\text{X}^-$ catalysts **2** in dilute solution (2.5 ml of toluene) at 80 °C. The results are given in Table 1. The precursor **2a** containing the weakly coordinating TfO^- anion led to a complete conversion of **3** after only 1 h at 80 °C and a 91% isolated yield of **4** was obtained. Moreover, when the same reaction was performed at room temperature for 19 h, the conversion reached 90% with exclusive formation of **4**. Consequently, catalyst precursor **2a** is the first example of a $[\text{Ru}=\text{C}=\text{C}=\text{CR}_2]$ complex able to perform the RCM reaction at room temperature with an excellent efficiency. It can be noted that the original precat-

Table 1 Activity of [(*p*-cymene)(PCy₃)ClRu=C=C=CPh₂]⁺X[−], **2**, in the RCM transformation **3** → **4**^a

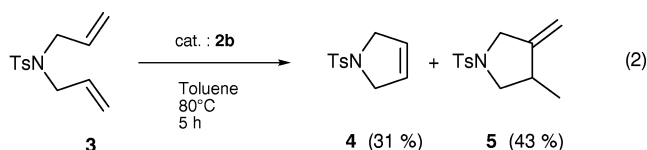
Precursor	X [−]	T/°C Heating period/h	Conversion /%	Yield of 4 / % ^b
2a	CF ₃ SO ₃ [−]	80/1	99	99 (91)
2a	CF ₃ SO ₃ [−]	r.t./19	90	90
2b	BF ₄ [−]	80/5	90	31 ^c
2b	BF ₄ [−] /2 Bu ⁿ ₄ NF	80/5	8	7.5
2b	BF ₄ [−] /4 Et ₂ O · BF ₃	80/4	99	96
2c	BPh ₄ [−]	80/5	91	91

^a 0.5 mmol of **3** in 2.5 ml of toluene with 2.5 mol% of precatalyst **2**.^b Yields determined by GC or isolated. ^c In addition to 43% of **5**.

talysts [(arene)(PR₃)ClRu=C=C=CPh₂][PF₆] containing the PCy₃ or PPr₃ⁱ ligand and the non-coordinating anion PF₆[−] exhibited poor catalytic activity below 80 °C.⁹

The efficiency of catalyst **2a** led us to perform both its formation and catalysis in one pot in order to study the ease of the process. Thus 1.3 × 10^{−2} mmol of [RuCl₂(*p*-cymene)]₂ and 2.8 × 10^{−2} mmol of PCy₃ were reacted in dichloromethane at room temperature for 1.5 h, then were added 1.04 equiv. of AgOTf and, after 1 h at room temperature, 1.1 equiv. of HC≡CC(Ph)₂OH. After 30 min of stirring at room temperature the dichloromethane was eliminated under vacuum, 5 ml of toluene and 40 equiv. of **3** were successively added. After 1 h at 80 °C the diene **3** was completely and selectively transformed, and the pyrrole **4** was isolated in 89% yield. In order to account for the activity of **2a** at room temperature, it can be suggested that the weakly coordinating TfO[−] anion should favour the dissociation of the *p*-cymene ligand, possibly *via* interaction with the allenylidene ligand, and stabilize the 14-electron species [CF₃SO₃...Ru=C=C=CPh₂(Cl)(PCy₃)]. Complex **2c** containing the bulky BPh₄[−] counter anion showed a catalytic activity only at 80 °C and thus is comparable with the precursor containing the PF₆[−] anion.⁹

It was surprising that the complex **2b** with the non-coordinating anion BF₄[−] led to a good conversion of **3** (90% at 80 °C for 5 h) (Table 1) but, in contrast to **1**⁹ and **2a**, afforded a low yield of **4** (31%). Actually, the reaction was not selective and besides **4**, 43% of the product **5** corresponding to the cyclization of **3** with atom economy¹⁰ was obtained:

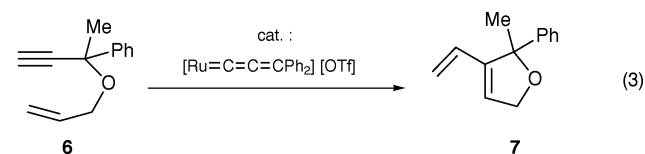


This type of cyclization with a 1,6-diene has already been observed with rhodium,¹¹ nickel,¹² and palladium^{11,13} catalysts but in the presence of an acid (HCl, AcOH or CF₃SO₃H) in order to generate a M–H bond.

As the anion BF₄[−] may release F[−] and BF₃, the influence of these reagents on the precatalyst **2b** has been studied in the transformation **3** → **4** + **5**. The addition of 2 equiv. of Buⁿ₄NF per equiv. of **2b** slowed down the reaction and after 4 h at 80 °C only **4** was formed in 7.5% yield (Table 1). This shows that the presence of fluoride dramatically inhibits the catalytic activity of **2b** towards RCM reaction. A similar inhibition was observed in the presence of the chloride anion. The addition of Et₂O · BF₃ to the reaction mixture of **3** and 2.5 mol% of **2b** increased the catalytic activity and the best results were obtained with the use of 10 mol% of Et₂O · BF₃ for 2.5 mol% of **2b**. At 80 °C, the reaction led to the complete conversion of **3** after 4 h and to the formation of 96% of **4** and only 3% of **5**.

Thus, the addition of the Lewis acid BF₃ to **2b** restores its catalytic activity towards the RCM reaction and leads to a decrease in the formation of **5**. One can make the hypothesis that BF₃ favours the displacement of the arene ligand allowing the RCM reaction. We have shown that traces of HBF₄ in the reaction mixture did not favour the formation of **5**, thus the formation of **5** may arise from initial oxidative coupling of the two C=C bonds of **3** at the Ru^{II} centre, followed by β-elimination and reductive elimination leading to the formation of the exocyclic H–CH₂ bond; this oxidative coupling is of course disfavoured by the presence of a Lewis acid.

The metathesis of ene-yne is also a powerful method for generating conjugated alkenyl cycloolefin derivatives such as cephem derivatives¹⁴ or N-containing heterocycles.¹⁵ The interest of vinyl-2,5-dihydrofurans for access to optically active derivatives *via* asymmetric catalysis¹⁶ led to the consideration of their general preparation *via* metathesis of ene-yne ethers in the presence of the most active triflate salt **2a**:



The ene-yne **6**, containing a hindered propargylic carbon atom was reacted in toluene in the presence of 2.5 mol% of **2a** at 80 °C. After 3 h, its transformation was completed and the 3-vinyl-2,5-dihydrofuran **7** was produced selectively and isolated in 82% yield. By contrast, the precatalyst [Ru=C=C=CPh₂][PF₆] is not so efficient as the total conversion of **6** into **7** required 24 h at 80 °C.¹⁷

This study not only shows that the 18-electron allenylidene ruthenium salts are efficient precatalysts for ring-closing metathesis of both dienes and ene-yne, but their activity dramatically depends on the nature of the counter anion, which can either control the reaction at room temperature (CF₃SO₃[−]) or create new catalytic reactions (BF₄[−]).

Acknowledgements

The authors wish to thank Professor A. Fürstner from the Max-Planck Institut für Kohlenforschung for stimulating discussions.

Notes and references

† Typical preparation of complex **2a**. 0.65 mmol of RuCl₂(PCy₃)(*p*-cymene) and 0.67 mmol of AgOTf were stirred at room temperature in 30 ml of dichloromethane for 1.5 h. After filtration, dichloromethane was removed by distillation under vacuum. The cationic complex [(*p*-cymene)RuCl(PCy₃)]⁺TfO[−] thus formed was washed with 20 ml of a (1 : 1) pentane–ether mixture and obtained as a brown powder [95%, ³¹P NMR: δ 28.33 (PCy₃)]. To 0.183 mmol of this cationic complex dissolved in 15 ml of dichloromethane was added 1.1 equiv. of HC≡CC(Ph)₂OH. After 1 h at room temperature, dichloromethane was eliminated under vacuum. The crude product was washed twice with 20 ml of diethyl ether to yield 155 mg (95%) of **2a** as a violet powder.

Complexes **2a–c** gave satisfactory IR and ¹H and ³¹P NMR spectroscopic analyses. Selected spectroscopic data: **2a** IR: ν 1963 cm^{−1} (Ru=C=C=C); ³¹P NMR (81.01 MHz, CDCl₃): δ 59.21 (PCy₃); **2b** IR: ν 1958 cm^{−1} (Ru=C=C=C); ³¹P NMR (81.01 MHz, CDCl₃): δ 59.08 (PCy₃); **2c** IR: ν 1960 cm^{−1} (Ru=C=C=C); ³¹P NMR (81.01 MHz, CDCl₃): δ 57.28 (PCy₃).

- Topics in Organometallic Chemistry, *Alkene Metathesis in Organic Synthesis*, ed. A. Fürstner, Springer Verlag, Berlin, 1998, vol. 1; K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, New York, 1997; R. H. Grubbs, S. J. Miller and G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446; M. Schuster and S. Blechert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2036; A. Fürstner, *Top. Catal.*, 1997, **4**, 285; S. K. Armstrong, *J. Chem. Soc.*,

- Perkin Trans. 1*, 1998, 371; R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413.
- 2 A. Fürstner and K. Langemann, *Synthesis*, 1997, 792; A. Fürstner and T. Müller, *J. Org. Chem.*, 1998, **63**, 424; R. Stragies and S. Blechert, *Synlett*, 1998, 169.
 - 3 G. D. Cuny, J. Cao and J. R. Hauske, *Tetrahedron Lett.*, 1997, **38**, 5237; G. D. Cuny and J. R. Hauske, *Chemtech*, 1998, **5**, 25; M. F. Schneider, N. Lucas, J. Velder and S. Blechert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 257.
 - 4 O. Fujimora and R. H. Grubbs, *J. Org. Chem.*, 1998, **63**, 824; J. P. A. Harrity, D. S. La, D. R. Cefalo, M. S. Visser and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1998, **120**, 2343; A. Fürstner and K. Langemann, *J. Am. Chem. Soc.*, 1997, **119**, 9130; C. M. Huwe, O. C. Kiehl and S. Blechert, *Synlett.*, 1996, 65.
 - 5 S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 9858.
 - 6 T. E. Wilhelm, T. R. Belderrain, S. N. Brown and R. H. Grubbs, *Organometallics*, 1997, **16**, 3867.
 - 7 J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab and M. Schulz, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1124.
 - 8 T. Weskamp, W. C. Schattenmann, M. Spiegler and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2490.
 - 9 A. Fürstner, M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, 1315.
 - 10 B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 259.
 - 11 R. Grigg, J. F. Malone, T. R. B. Mitchell, A. Ramasubbu and R. M. Scott, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1745.
 - 12 B. Bogdanovic, *Adv. Organomet. Chem.*, 1979, **17**, 105; G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1988, **37**, 185.
 - 13 For a review on transition metal catalyzed cycloisomerizations, see: B. M. Trost and M. J. Krische, *Synlett*, 1998, 1.
 - 14 A. G. Barrett, S. P. D. Baugh, D. C. Braddock, K. Flack, V. C. Gibson and P. A. Procopiou, *Chem. Commun.*, 1997, 1375.
 - 15 A. Kinoshita and M. Mori, *Synlett*, 1994, 1020; A. Kinoshita and M. Mori, *J. Org. Chem.*, 1996, **61**, 8356.
 - 16 M. T. Didiuk, C. W. Johannes, J. P. Morken and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1995, **117**, 7097.
 - 17 M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, 2249.

Paper 8/08859D