Letter

Room temperature operating allenylidene precatalyst $[L_nRu{=}C{=}C{=}CR_2]^+X^-$ for olefin metathesis: dramatic influence of the counter anion X^-

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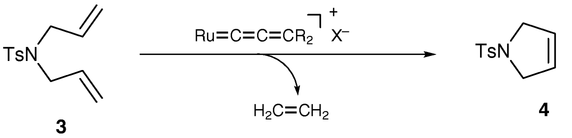
The allenylidene-ruthenium(II) complex $[(p\text{-cymene})(PCy_3)ClRu{=}C{=}C{=}CPh_2]^+X^-$, 2a, ($X^- = CF_3SO_3^-$), which is produced in a one-pot reaction from commercially available $[RuCl_2(p\text{- cymene})]_2$, catalyses the ring-closing metathesis of *N,N*-diallyltosylamide at room temperature whereas 2b ($X^- = BF_4^-$) favours the cyclization of the 1,6-diene 3 into the five-membered heterocycle 5 without loss of atoms. The addition of $BF_3 \cdot OEt_2$ 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 $Cl_2(PCy_3)_2Ru{=}CHR$.[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 $Ru{=}CHR$ moiety and bulky phosphines[6,7] or carbene ligands.[8] Recently, it was found that the 18-electron cationic allenylidene complexes of the type $[(arene)(PR_3)ClRu{=}C{=}C{=}CPh_2][PF_6]$,[9] containing only one bulky phosphine ($PR_3 = PCy_3$, PPr^i_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 $[Cl_2(PCy_3)_2Ru{=}CHR]$ complexes.[5] The efficiency of these cationic precatalysts raises, however, the question of the influence of the counter anion.

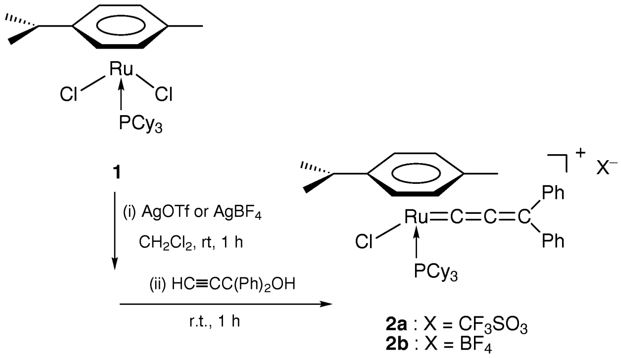
Now we report (*i*) the first example of an allenylidene precatalyst able to perform the RCM reaction at room temperature, namely the derivative $[(p\text{-cymene})(PCy_3)ClRu{=}C{=}C{=}CPh_2][O_3SCF_3]$, **2a**, prepared in a one-pot reaction from commercially available $[RuCl_2(p\text{-cymene})]_2$ and *via* $RuCl_2(PCy_3)(p\text{-cymene})$ **1**, (*ii*) evidence for the unexpected dramatic influence of the counter anion X^- on the catalytic activity of the $[L_nRu{=}C{=}C{=}CPh_2][X]$ 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 $[(arene)(PR_3)ClRu{=}C{=}C{=}CPh_2]^+X^-$, **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:



(1)

The precursors **2a** ($X^- = CF_3SO_3^-$) and **2b** ($X^- = BF_4^-$) were obtained by treatment of the complex $RuCl_2(PCy_3)(p\text{-cymene})$, **1**, with a slight excess of AgOTf or $AgBF_4$ in dichloromethane at room temperature to generate *in situ* the isolatable 16-electron intermediate $[(p\text{-cymene})(PCy_3)ClRu]^+X^-$. The addition to the latter of an excess of $HC{\equiv}CC(Ph)_2OH$ in dichloromethane led to the isolation of fully characterized **2a** and **2b** in 95% yields (Scheme 1).† $[(p\text{-cymene})(PCy_3)ClRu]^+[BPh_4]^-$, **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 $HC{\equiv}CC(Ph)_2OH$.†



Scheme 1

The transformation of **3** (0.5 mmol) into **4** was performed with 2.5 mol% of isolated $[Ru{=}C{=}C{=}CPh_2]^+X^-$ 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 $[Ru{=}C{=}C{=}CR_2]$ complex able to perform the RCM reaction at room temperature with an excellent efficiency. It can be noted that the original preca-

Table 1 Activity of [(p-cymene)(PCy_3)ClRu=C=C=CPh_2]$^+X^-$, **2**, in the RCM transformation **3** → **4**[a]

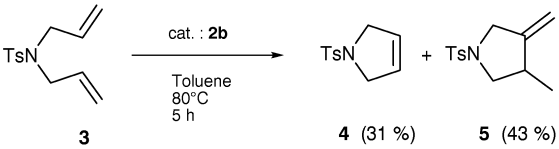
Precursor	X^-	T/°C Heating period/h	Conversion /%	Yield of **4**/%[b]
2a	$CF_3SO_3^-$	80/1	99	99 (91)
2a	$CF_3SO_3^-$	r.t./19	90	90
2b	BF_4^-	80/5	90	31[c]
2b	BF_4^-/2 Bu^n_4NF	80/5	8	7.5
2b	BF_4^-/4 $Et_2O \cdot BF_3$	80/4	99	96
2c	BPh_4^-	80/5	91	91

[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)(PR_3)ClRu=C=C=CPh_2][PF_6] containing the PCy_3 or PPr^i_3 ligand and the non-coordinating anion PF_6^- 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 [$RuCl_2$(p-cymene)]$_2$ and 2.8×10^{-2} mmol of PCy_3 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≡C$(Ph)_2$OH. 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 [CF_3SO_3···Ru=C=C=CPh_2(Cl)(PCy_3)]. Complex **2c** containing the bulky BPh_4^- counter anion showed a catalytic activity only at 80 °C and thus is comparable with the precursor containing the PF_6^- anion.[9]

It was surprising that the complex **2b** with the non-coordinating anion BF_4^- 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 economy[10] was obtained:

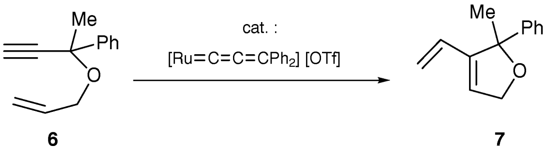


(2)

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 CF_3SO_3H) in order to generate a M—H bond.

As the anion BF_4^- may release F^- and BF_3, the influence of these reagents on the precatalyst **2b** has been studied in the transformation **3** → **4** + **5**. The addition of 2 equiv. of Bu^n_4NF 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 $Et_2O \cdot BF_3$ 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 $Et_2O \cdot BF_3$ 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 BF_3 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 BF_3 favours the displacement of the arene ligand allowing the RCM reaction. We have shown that traces of HBF_4 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—CH_2 bond; this oxidative coupling is of course disfavoured by the presence of a Lewis acid.

The metathesis of ene-ynes is also a powerful method for generating conjugated alkenyl cycloolefin derivatives such as cephem derivatives[14] or N-containing heterocycles.[15] The interest of vinyl-2,5-dihydrofurans for access to optically active derivatives *via* asymmetric catalysis[16] led to the consideration of their general preparation *via* metathesis of ene-yne ethers in the presence of the most active triflate salt **2a**:



(3)

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=CPh_2][PF_6] 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-ynes, but their activity dramatically depends on the nature of the counter anion, which can either control the reaction at room temperature ($CF_3SO_3^-$) or create new catalytic reactions (BF_4^-).

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Notes and references

† Typical preparation of complex **2a**. 0.65 mmol of $RuCl_2(PCy_3)$(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 vaccum. The cationic complex [(p-cymene)RuCl(PCy_3)]$^+TfO^-$ thus formed was washed with 20 ml of a (1 : 1) pentane–ether mixture and obtained as a brown powder [95%, ^{31}P NMR: δ 28.33 (PCy_3)]. To 0.183 mmol of this cationic complex dissolved in 15 ml of dichloromethane was added 1.1 equiv. of HC≡C$(Ph)_2$OH. 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 ^{31}P NMR spectroscopic analyses. Selected spectroscopic data: **2a** IR: ν 1963 cm^{-1} (Ru=C=C=C); ^{31}P NMR (81.01 MHz, $CDCl_3$): δ 59.21 (PCy_3); **2b** IR: ν 1958 cm^{-1} (Ru=C=C=C); ^{31}P NMR (81.01 MHz, $CDCl_3$): δ 59.08 (PCy_3); **2c** IR: ν 1960 cm^{-1} (Ru=C=C=C); ^{31}P NMR (81.01 MHz, $CDCl_3$): δ 57.28 (PCy_3).

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