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New air-stable ruthenium olefin metathesis precatalysts derived from bisphenol S

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Abstract

Synthesis and screening of catalytic activity of novel mono- and diruthenium carbene complexes **7a** and **7b** prepared from inexpensive Bisphenol S via Claisen rearrangement–isomerisation route is described. These catalysts constitute an excellent tool for ring-closing metathesis by combining high stability with increased catalytic activity as compared with the parent Hoveyda–Grubbs catalyst.

Keywords: Ruthenium; Metathesis; Catalysis; C–C bond forming reaction; Carbene complex

1. Introduction

Finding of a subtle balance between the stability of the catalyst (and its insensitivity to impurities), and its high activity has been called one of the "Holy Grails" of catalysis. This is especially visible in the field olefin metathesis: a fairly old reaction that has long remained as laboratory curiosity without significance for advanced organic chemistry [1]. New organometallic catalysts which combine high catalytic activity with fairly good stability, however, have revolutionized the field, as witnessed by the mushrooming number of metathesis publications [2,3]. This is largely due to discovery of active, well-defined first-generation ($(PCy_3)_2Cl_2Ru{=}CHPh$), second-generation **1a** and third-generation **1b** ruthenium carbene complexes at Caltech [4–6].

At the same time, new metathesis catalysts are being developed to extend the scope of the reaction to substrates for which the traditional catalyst systems were not adequate. Hoveyda et al. have prepared chromatography and air-stable complex **1c** [7a]. Later the second-generation version of this chelate (**1d**) has been reported by Hoveyda [7b,8] and Blechert [9]. Despite lower initiation activity exhibited by phosphine-free **1d**, as compared with Grubbs' catalysts **1a** and **1b**, its use was proved to be advantageous in many cases, particularly in reactions of electron-deficient olefins [8,9]. Our group has recently introduced the 5-nitro-substituted analogue **1e** which was shown to exhibit impressive activity in ring-closing (RCM), cross (CM) and enyne-metathesis while retaining excellent air and thermal stability [10–12]. As a result, catalyst **1e** has found a successful application in target oriented syntheses and in the pharmaceutical industry [13–16].

In the case of Hoveyda–Grubbs complexes initiation requires dissociation of the aryl ether ligand as well as a

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metathesis step [8]. The slower rate of initiation of **1d** is likely due to the less facile dissociation of the bidentate ligand from the metal centre. The higher activity of **1e** may be the result of faster initiation of the catalytic cycle due to a more facile release of the electron deficient substituted benzylidene ligand. We proposed that the nitro group present in the benzylidene fragment of **1e** weakens O → Ru chelation and facilitates *faster initiation* of the catalytic cycle [10]. In addition, the *suppression of oxygen reassociation* to the Ru centre caused by a electron-withdrawing group (EWG) and the increased electron deficiency at the initiating carbene species should make these complexes more active in olefin metathesis [10,17].

In this article we disclose details of the syntheses and catalytic activities of two new Hoveyda-type complexes **7a** and **7b**, which initiation efficiency is enhanced by the introduction of the electron-withdrawing SO_2 group.

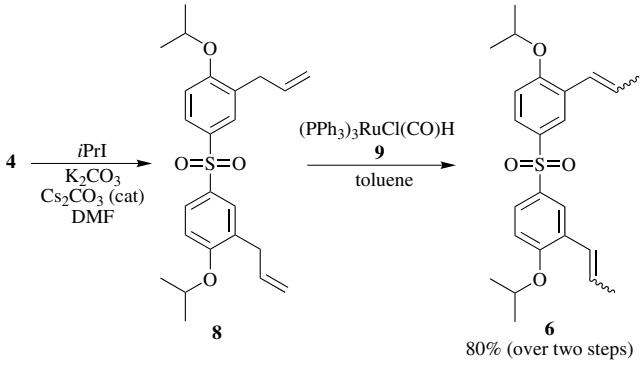
2. Results and discussion

Following our concept of destabilizing the Ru–O bond in order to favour the ether decoordination that generates the catalytically active 14-electron species, we decided to synthesize a sulfone-substituted Hoveyda-type catalyst. We envisaged that commercially available 4,4′-dihydroxydiphenyl sulfone **2** (Bisphenol S), an inexpensive chemical used for various plastics and resins, as well as in textile auxiliaries, tanning agents, photographic coupling agents and thermo paper dyes, can be a convenient starting material in our synthesis. Application of the general methodology developed in our group [18] should give a direct access to a "dimeric" catalyst **7** [19] in which two Hoveyda-type ligands are connected via the SO_2 bridge (Schemes 1 and 3). Indeed, allylation of **2** followed by Claisen rearrangement led to compound **4** [20]. For isomerisation of C–C double bonds, conditions previously developed in our group were used [18] leading to the precursor **6** in good yield (Scheme 1).

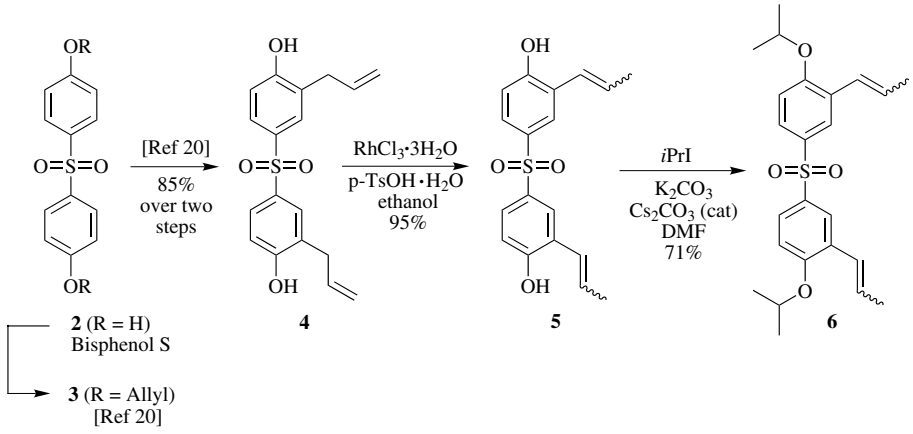
To avoid using relatively large amounts of rhodium (10 mol%, Scheme 1), which were required for complete isomerisation of both C–C double bonds of **4**, we searched for another isomerisation conditions. From a variety of reagents [18], the ruthenium hydride complex $(PPh_3)_3RuCl(CO)H$ (**9**) was chosen [21]. The incompatibility of **9** with acidic phenol groups enforced us to introduce *i*Pr ether prior to isomerisation step (Scheme 2). This small redesign of our initial synthesis strategy profited by enhancing its efficiency, as only 1.5 mol% of **9** was enough to allow full conversion of crude **8** into **6** (80% of isolated yield over two steps), making $(PPh_3)_3RuCl(CO)H$ the catalyst of choice in this transformation (Scheme 2).

Having secured access to a benzylidene ligand precursor, we attempted to prepare catalysts **7**. We established that, as depicted in Scheme 3, treatment of **1a** with 3 equiv of **6** and 3 equiv of CuCl in CH_2Cl_2 at 40 °C delivers mono-ruthenium complex **7a** as a deep green solid in 86% yield after silica gel chromatography on air. Use of 2 equiv of **6** led to the formation of the bis-ruthenium complex **7b** as a second product. In order to obtain better yield of **7b**, 2 equiv of the Grubbs' catalyst **1a** per one equivalent of **6** have to be used. Under these conditions, the major product **7b**, easily separable from **7a** by column chromatography, was obtained as a deep green solid in 66% yield.

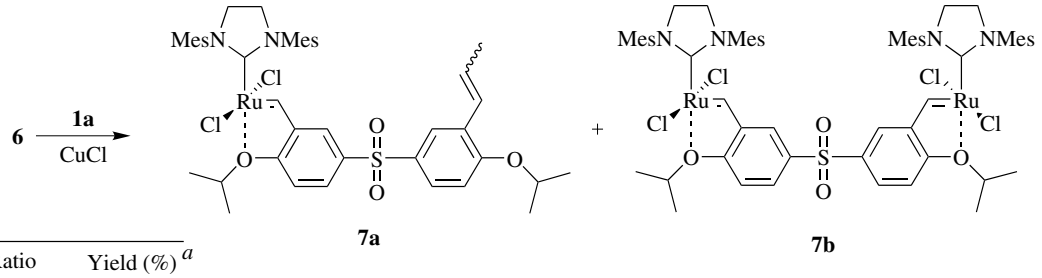
Both ruthenium carbenes, **7a** and **7b**, possess very good air, moisture, and thermal stability and can be handled in



Scheme 2. Alternative synthesis of precursor **6**.



Scheme 1. Preparation of a ligand precursor **6**.



Ratio	Yield (%) [a]
1a : **6**	**7a** : **7b**
1 : 3	86 : 0
1 : 2	78 : 17
2 : 1	21 : 66

Scheme 3. Preparation of catalysts **7a** and **7b**. Isolated yields after column chromatography.

air and stored for extended periods of time (several months at +4 °C) without decomposition or diminishing of their activity. In the case of **7b** it was possible to obtain crystals suitable for X-ray structure analysis. Molecules of **7b** (Fig. 1) crystallise from CH_3OH/CH_2Cl_2 in the triclinic P-1 space group, with one molecule in the independent part of the unit cell. The complex occupies a general position, although it looks like being symmetric with 2-fold axis passing through the central sulfur atom of the SO_2 group. Monocrystals of this compound contain significant amount of solvent molecules (four CH_3OH molecules per one **7b** moiety) located asymmetrically with relation to the central host fragment. The solvent molecules disappear immediately from monocrystals when one takes the monocrystals out of the mother solution [22]. The two Ru centres in **7b** are separated ca. 10.7 Å apart. We do not see any significant differences between these two metal centres. Both of them exhibit tetragonal coordination with very much similar bond lengths and valence angles. The most important parameters describing geometry of the metal ions and their nearest atomic fragments are given in Table 1.

The molecules of **7b**—consisting of the two almost symmetric and topologically identical molecular fragments—are folded in the crystal lattice (Figs. 2 and 3). In fact, the molecules of **7b** form channels passing through the whole crystal lattice. Two molecules of **7b** forms a kind of a local void surrounded by some bulky substituents. As can be seen in Fig. 3, the molecules nicely fit one into another forming channels in two dimensions.

Having these new complexes in hand, we decided to study their catalytic activity. For such comparative investigation, we chose a model RCM reaction of diene **10a**, leading to the formation of cyclic product **11** bearing a trisubstituted double bond (Table 2). The results, illustrated in Fig. 4, reveal that both catalysts **7a** and **7b** are significantly more reactive than parent Hoveyda catalyst **2b**. Interestingly, the bis-ruthenium complex **7b** (0.5 mol% which is equivalent to 1.0 mol% Ru) initializes the reaction visibly faster than mono-ruthenium **7a** used in the same amount (1.0 mol%; Fig. 4). Next, we attempted to test the recyclability of the mono-ruthenium complex **7a**. One of the unique properties of Hoveyda carbene **2c** is that up to 95% of the catalyst can be recovered after the reaction [7]. However, except for **1e** [11], no data are available regarding the recyclability of the electronically- or sterically-activated [17] Hoveyda-type catalysts. We surmised that the presence of the additional chelating site in **7a**

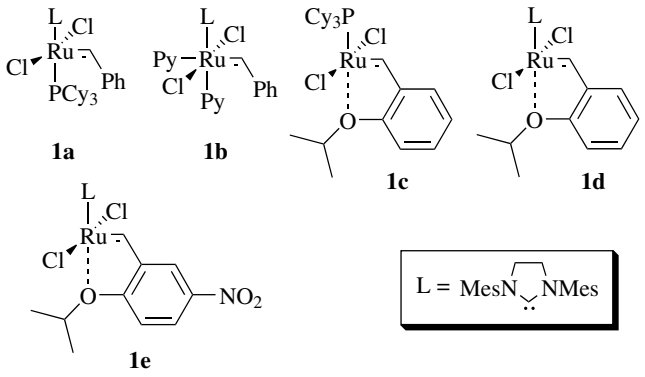


Fig. 1. Selected ruthenium precatalysts for olefin metathesis. Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl.

Table 1
Selected bond lengths (Å) and angles (°) for **7b**

Ru(1)–C(7)	1.808(14)
Ru(1)–C(11)	1.971(14)
Ru(1)–O(3)	2.291(9)
Ru(1)–Cl(2)	2.331(4)
Ru(1)–Cl(1)	2.346(4)
Ru(2)–C(38)	1.844(13)
Ru(2)–C(42)	1.988(13)
Ru(2)–O(4)	2.273(8)
Ru(2)–Cl(4)	2.325(4)
Ru(2)–Cl(3)	2.345(4)
C(7)–Ru(1)–C(11)	101.8(6)
C(7)–Ru(1)–O(3)	78.9(5)
C(11)–Ru(1)–O(3)	174.7(5)
Cl(2)–Ru(1)–Cl(1)	159.9(1)
C(38)–Ru(2)–C(42)	100.6(5)
C(38)–Ru(2)–O(4)	79.3(5)
C(42)–Ru(2)–O(4)	179.6(5)
Cl(4)–Ru(2)–Cl(3)	158.5(1)

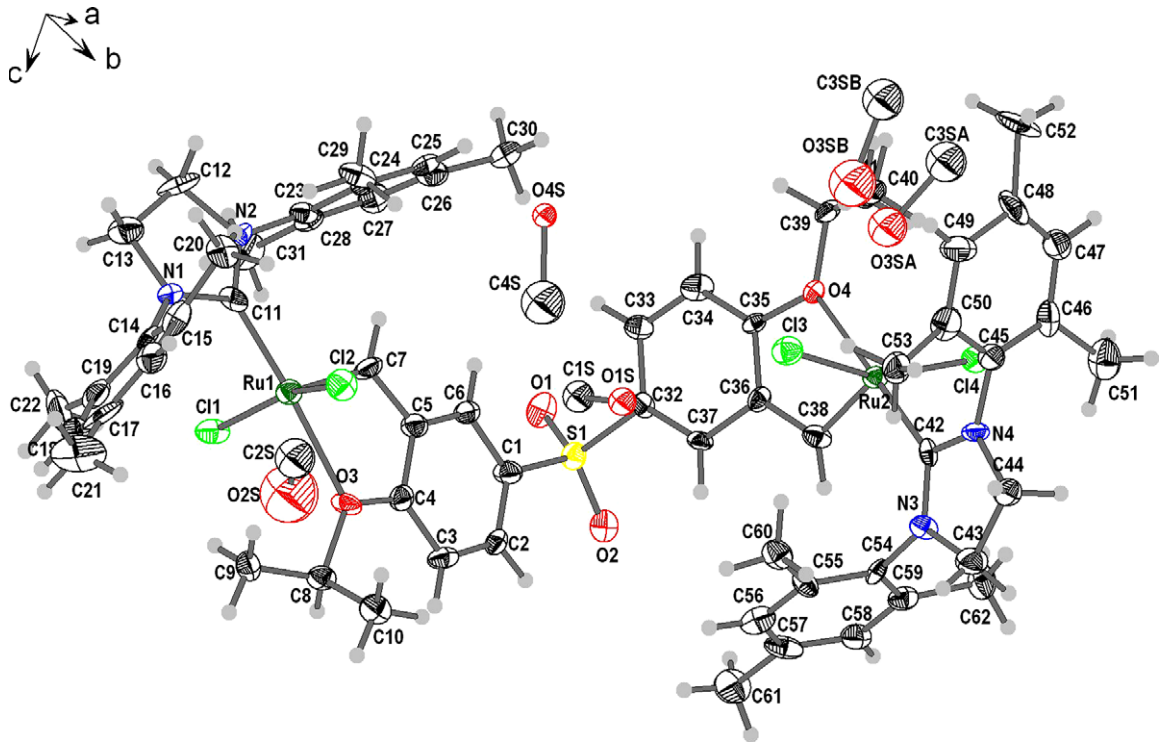


Fig. 2. Structure of **7b** with the solvent molecules included (CH_3OH). The hydrogen atom labels are excluded for clarity.

would lead to a more effective recoordination of active Ru-species [19]. To answer this question, we attempted to isolate **7a** after two model RCM and one enyne reaction [15].

Data presented in Table 2 confirm the general very good reactivity of these new catalysts. However, the recyclability of **7a** is similar to that of the nitro-Hoveyda catalyst **2e** [11], and typically **7a** can be recovered after metathesis reaction with moderate efficiency (43–73%).

An interesting application of metathesis has been recently published by Boehringer Ingelheim Ltd. in the synthesis of BILN 2061, the first reported Hepatitis C Virus (HCV) NS3 protease inhibitor to have shown an antiviral effect in infected humans. The HCV infection is a serious cause of chronic liver disease worldwide. The macrocyclic peptide, BILN 2061, is the first compound of its class to have reached clinical trials. It has shown oral bioavailability and antiviral effect in humans infected with HCV [23] The key step in the preparation of BILN 2061 is the RCM formation of the 15-membered ring (Scheme 4) [24]. The first generation Hoveyda's catalyst **1c** (Fig. 1) was used for preparation of almost 400 kg of the macrocyclic intermediate **13**, proving its feasibility and usefulness for the production of pharmaceutical compounds [25]. However, relatively high catalyst loadings (up to 3 mol% relative to the diene **12**) was required to achieve complete conversions within 3–4 h [25]. Therefore, new more reactive catalysts, such as **1e** are being investigated with the aim to shorten the reaction times and to reduce the catalyst loading [25,26]. We decided to extend this study to the newly obtained EWG-activated, yet very stable catalysts **7a** and 7b. In a comparative experiment the catalyst (equivalent to 0.4 mol% Ru) was added to the degassed toluene solution of diene **12** and the reaction mixture was stirred at 80 °C for 60 min. After this time a second portion of the catalyst (0.2 mol% Ru) was added and the reaction was continued for the next 60 min. The progress of the reaction was monitored by HPLC.

As it can be seen from data presented on Scheme 4 and Figure both sulfone-bearing complexes **7a** and **7b** gave good results in the cyclization of macrocyclic ring of BILN 2061. Loadings as low as 0.4 mol% of **7a** were sufficient to obtain 70% of conversion in less than 10 min, addition of a second portion of the catalyst (to total Ru 0.6 mol%) allowed to reach 90% of conversion in 70 min. The bis-ruthenium catalyst **7b** was even more efficient, giving practically quantitative conversion after the same time (Fig. 5).

3. Conclusions

The results obtained during our previous research witnessed that the Hoveyda-type catalysts can be significantly improved by changing the electronic situation in the benzylidene ligand [10]. This notion has strong implications for catalyst design. In this paper, we reported that the SO_2 group increases catalytic activity the Hoveyda-type catalyst **7a** and **7b** by destabilizing the Ru–O chelation. At the same time this group can be used as a bridge connecting two 2-isopropoxy-benzylidene fragments, to yield a "dimeric" catalyst **7b**. These new, stable and easy to obtain from inexpensive Bisphenol S complexes are also

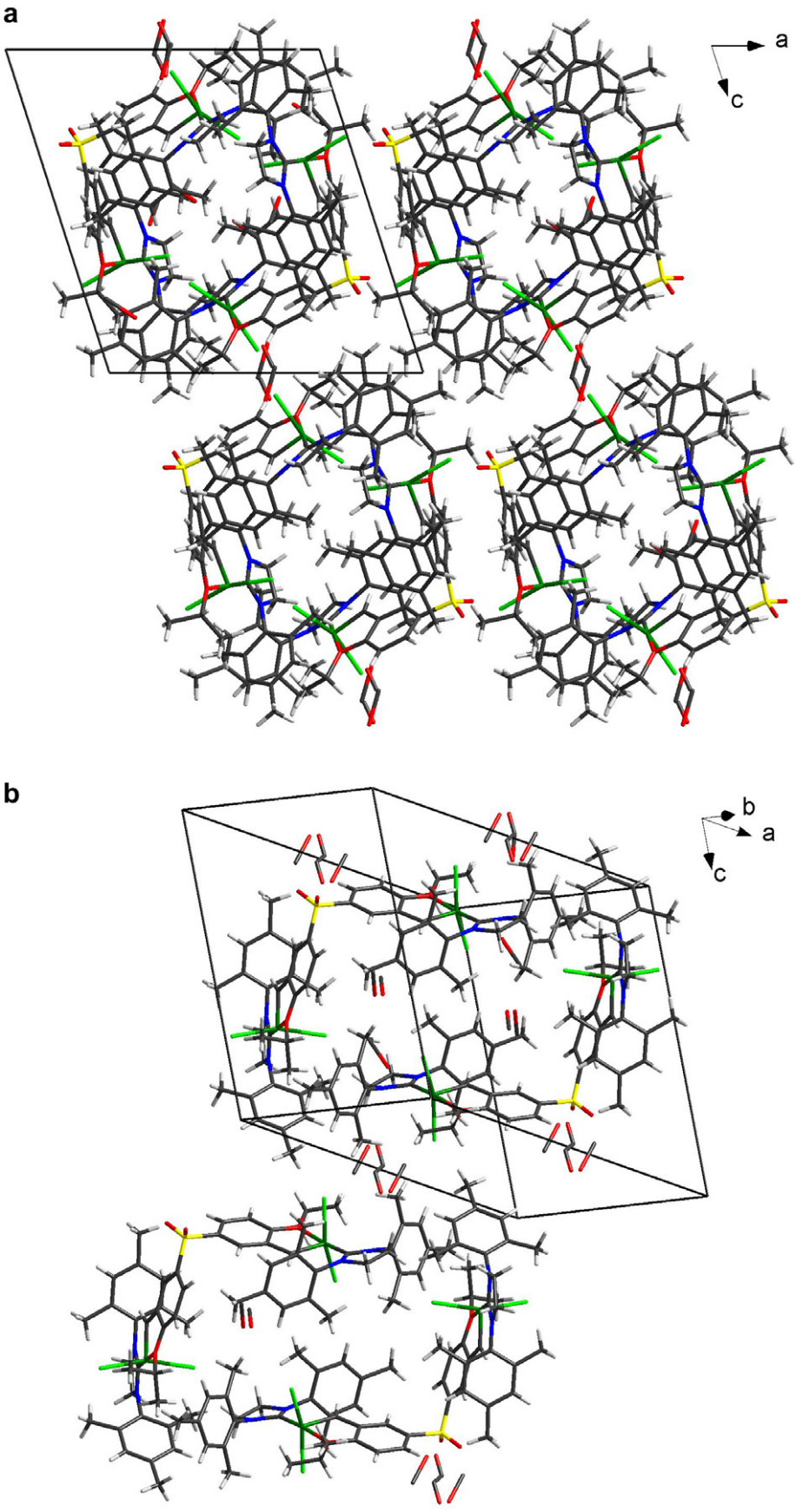
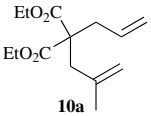
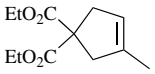
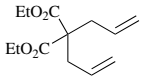
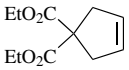
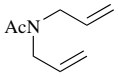
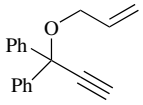
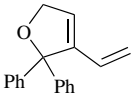


Fig. 3. Projection of the crystal lattice of **7b** along the Y-axis (a), and cavities form by molecules of **7b** (b).

Table 2
Catalytic activity of **1d**, **7a** and **7b** in RCM reactions of model substrates

Substrate **10**	Product **11**	Catalyst (mol%)	Temperature (°C); time	Yield[a] (%)	Regenerated catalyst (%)
 **10a**	 **11a**	**7a** (1.0) **7b** (1.0) **7b** (0.5) **1d** (1.0)	26; 5 h	90 98 91 62	n.d.
 **10b**	 **11b**	**7a** (2.5)	20; 2 h	99	43
 **10c**	 **11c**	**7a** (2.5)	20; 20 min	99	64
 **10d**	 **11d**	**7a** (2.5)	0; 1 h	99	73

[a] Yield according to GC; n.d. = not determined.

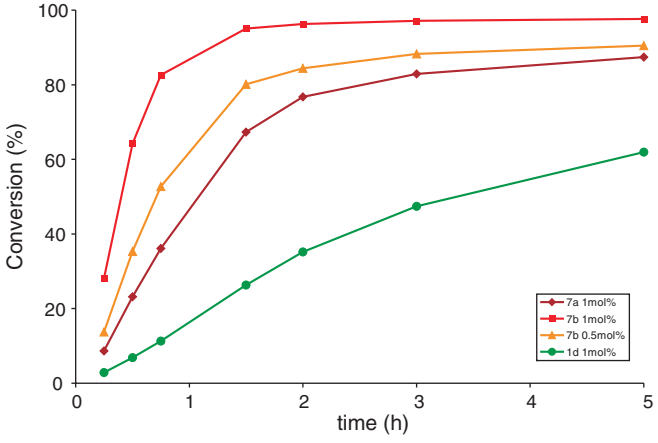


Fig. 4. Activity of **1d**, **7a** and **7b** in RCM of **10a** in dichloromethane, 26 °C, 5 h; conversions according to GC.

attractive from practical point of view, as they gave very good results in preparation of an important pharmaceutical compound.

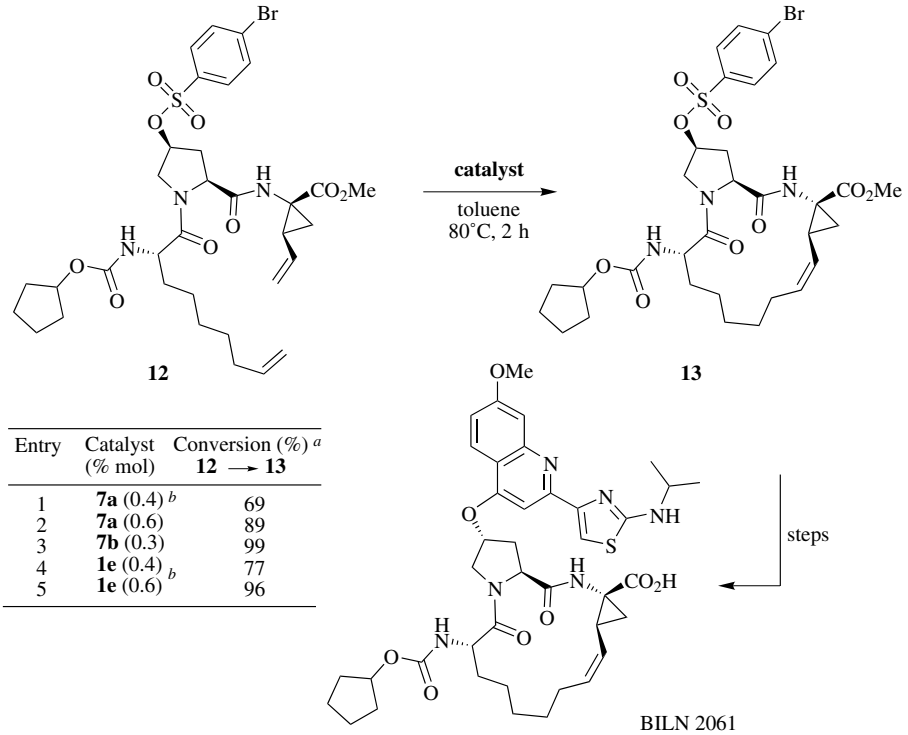
4. Experimental

4.1. Materials

Ruthenium carbenes **1a**, **1c–d** and other reagents were purchased from Aldrich or Fluka. Catalyst **1e** [10,11] and the precursor **5** [18b,18c] were prepared according to literature procedures. Cesium carbonate was a gift from Chemetall GmbH. Toluene was dried by azeotropic distillation and degassed by bubbling nitrogen. CH_2Cl_2 and DMF were dried with CaH_2 and distilled prior to use.

4.2. Preparation of the ligand precursor **6**

A dry powdered K_2CO_3 (0.581 g, 4.2 mmol), Cs_2CO_3 (0.142 g, 0.4 mmol) and **5** (0.341 g, 1.0 mmol) and dry DMF (5 mL) were placed in a round bottom flask. The mixture was stirred about 5 min and isopropyl iodide (430 μL, 4.2 mmol) was added dropwise. The resulted mixture was stirred for 24 h at 35 °C. Water (10 mL) was added and the mixture was extracted with AcOEt (3 × 25 mL). Combined extracts were dried and evaporated to dryness. The crude product was purified by column chromatography (20% EtOAc in *c*-hexane) to give product **6** (0.303 g, 71%), as a colourless low melting solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (d, $^3J_{HH} = 6.0$ Hz, 12H, CH_3), 1.90 (dd, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 1.7$ Hz, 6H, CH_3), 4.59 (k, $^3J_{HH} = 6.0$ Hz, 2H, C_2CH), 6.31 (dq, $^3J_{HH} = 15.9$ Hz, $^3J_{HH} = 6.6$ Hz, 2H, CH), 6.63 (dq, $^3J_{HH} = 15.9$ Hz, $^4J_{HH} = 1.7$ Hz, 2H, CH), 6.87 (d, $^3J_{HH} = 9.0$ Hz, 1H, Ar–H), 7.69 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.4$ Hz, 2H, Ar–H) 7.93 (d, $^4J_{HH} = 2.4$ Hz, 2H, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 21.9, 70.7, 112.8, 124.5, 125.8, 127.2, 128.4, 133.4, 157.8; MS EI: *m*/*z* (%) 417 (3), 416 (16), 415 (46), 414 (100, $M^{+\cdot}$), 372 (14), 331 (11), 330 (52), 328 (9), 181 (12), 149 (9), 133 (10), 131 (9), 57 (10), 43 (18), 41 (16); IR (film, cm^{-1}); *v* 2979, 2932, 2875, 2855, 1686, 1650, 1590, 1481, 1451, 1412, 1386, 1375,



Entry	Catalyst (% mol)	Conversion (%) [a] 12 → 13
1	**7a** (0.4) [b]	69
2	**7a** (0.6)	89
3	**7b** (0.3)	99
4	**1e** (0.4) [b]	77
5	**1e** (0.6)	96

Scheme 4. Comparative study of catalysts **1e**, **7a** and **7b** activity in cyclization of BILN 2061 precursor **12**. Reaction conditions: 0.3–0.6 mol% of catalyst, toluene, 80 °C, 2 h. [a] Conversion determined by HPLC after 2 h. [b] Conversion determined by HPLC after 1 h.

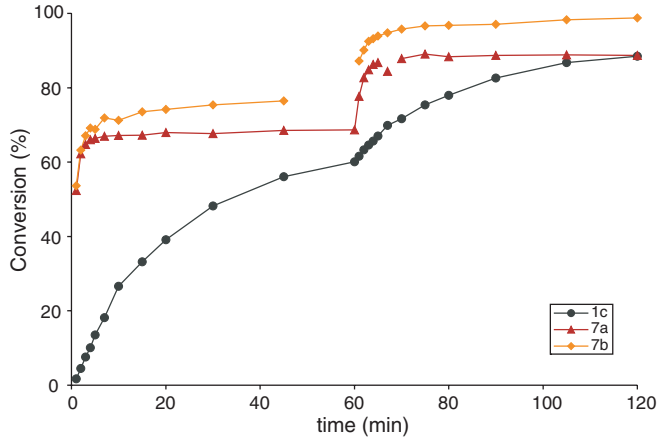


Fig. 5. Activity of **1c**, **7a** and **7b** in RCM of **12** in toluene, 80 °C, 2 h; catalysts were added in two portions (0.4 + 0.2 mol% Ru). Conversions according to HPLC.

1314, 1255, 1188, 1156, 1121, 1105, 1083, 968, 948, 902, 820, 756, 700, 607, 532; HR MS (EI) calc. for $[M]^{+\cdot}$: $C_{24}H_{30}O_4S$: 414.18648; found: 414.18615.

4.3. Preparation of precatalyst *7a*

Compound **6** (193.6 mg; 0.47 mmol), CuCl (20.1 mg; 0.20 mmol) and CH_2Cl_2 (8 mL) were placed in a Schlenk flask. Afterwards carbene complex **1a** (125.8 mg; 0.15 mmol) was added and the resulted solution was stirred under argon at 40 °C for 20 min. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and the resulted material was purified by column chromatography on silica. Elution with *c*-hexane:AcOEt (9:1) removes **7a** as a green band. The solvent was evaporated and product dissolved in a small amount CH_2Cl_2, then MeOH was added and slowly evaporated until green crystals precipitated. The precipitate was filtered off, washed with *n*-pentane and dried in vacuo to afford complex **7a** (110.7 mg, 86%) as green crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (d, $^3J_{HH} = 6.1$ Hz, 6H, CH_3), 1.37 (d, $^3J_{HH} = 6.0$ Hz, 6H, CH_3), 1.93 (d, $^3J_{HH} = 6.7$ Hz, 3H, CH_3), 2.44 (bs, 18H, $ArCH_3$), 4.19 (s, 4H, CH_2); 4.62 (k, $^3J_{HH} = 6.0$ Hz, 1H, C_2CH), 4.91 (k, $^3J_{HH} = 6.1$ Hz, 1H, C_2CH), 6.32 (dq, $^3J_{HH} = 15.9$ Hz, $^3J_{HH} = 6.7$ Hz, 1H, CH), 6.66 (d, $^3J_{HH} = 15.9$ Hz, 1H, CH), 6.84 (d, $^3J_{HH} = 8.7$ Hz, 1H, Ar–H), 6.89 (d, $^3J_{HH} = 8.7$ Hz, 1H, Ar–H), 7.06 (s, 4H, Ar–H), 7.43 (d, $^4J_{HH} = 2.0$ Hz, 1H, Ar–H), 7.60 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.2$ Hz, 1H, Ar–H), 7.90 (d, $^4J_{HH} = 2.2$ Hz, 1H, CH_3), 8.04 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, Ar–H), 16.39 (s, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.8, 19.3, 21.0, 21.9, 51.5, 53.4, 71.0, 76.8, 113.1, 113.2, 121.6, 124.6, 126.1, 127.5, 128.0, 128.4, 128.8, 129.4, 132.5, 136.6, 139.1, 144.7, 154.9, 158.2, 209.2, 292.6 (C=Ru); MS (ESI (+); MeOH/CH_2Cl_2), The molecular formula was confirmed by comparing the theoretical and experimental isotope patterns for $[M]^{+\cdot}$ ion ($C_{43}H_{52}Cl_2N_2O_4RuS$) found to be identical within the experimental error limits; IR (film, cm^{-1}); *v* 3437 (w), 2977 (m), 2914 (m), 1581 (m), 1481

(s), 1446 (m), 1420 (m), 1308 (m), 1259 (s), 1155 (m), 1125 (s), 1083 (s), 967 (w), 935 (m), 851 (w), 817 (w), 724 (w), 699 (m), 602 (s), 534 (m).

4.4. Preparation of precatalyst 7b

Precursor **6** (44.9 mg; 0.11 mmol), CuCl (27.3 mg; 0.27 mmol) and CH_2Cl_2 (10 mL) were placed in a Schlenk flask. Afterwards carbene complex **1a** (194.2 mg; 0.23 mmol) was added and the resulted solution was stirred under argon at 40 °C for 30 min. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and the resulted material was purified by column chromatography on silica. Elution with *c*-hexane:AcOEt (9:1) removes first **7a** as a green band and afterwards **7b** as a green band as well. The solvent was evaporated and each of two fractions was dissolved in a small amount CH_2Cl_2, then MeOH was added and slowly evaporated until green crystals precipitated. The precipitate was filtered off, washed with *n*-pentane and dried in vacuo to afford complex **7a** (19.2 mg, 21%) as green crystals and the main product **7b** (94.3 mg, 66%) as green crystals. Complex **7b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (d, $^3J_{HH} = 6.0$ Hz, 12H, CH_3), 2.41 (bs, 12H, $ArCH_3$), 2.46 (bs, 24H, $ArCH_3$), 4.19 (s, 8H, CH_2); 4.93 (k, $^3J_{HH} = 6.0$ Hz, 2H, C_2CH), 6.87 (d, $^3J_{HH} = 8.7$ Hz, 2H, Ar–H), 7.07 (s, 8H, Ar–H), 7.52 (s, 2H, Ar–H), 7.87 (d, $^3J_{HH} = 8.7$ Hz, 2H, Ar–H), 16.41 (s, 2H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.3, 21.0, 21.1, 51.5, 113.5, 121.4, 128.7, 129.5, 135.4, 139.1, 144.5, 155.2, 209.1, 292.0 (C=Ru); MS (ESI (+); MeOH/CH_2Cl_2) the molecular formula was confirmed by comparing the theoretical and experimental isotope patterns for $[M]^+$ ion ($C_{62}H_{74}Cl_4N_4O_4Ru_2S$) found to be identical within the experimental error limits; IR (film, cm^{-1}); *v* 3444 (m), 2917 (m), 1606 (w), 1572 (m), 1480 (s), 1420 (s), 1398 (s), 1262 (s), 1131 (s), 1086 (s), 939 (m), 916 (m), 852 (m), 723 (w), 702 (m), 613 (m), 589 (s), 532 (w).

4.5. Catalytic RCM of 10a with 7a and 7b

To a solution of catalyst **7a** or **7b** (0.01–0.005 mmol, 1.0–0.5 mol%) in CH_2Cl_2 (40 ml) in a Schlenk tube a solution of diene **10a** (1.0 mmol) was introduced in CH_2Cl_2 (5 ml) and the reaction mixture was stirred for 5 h at 26 ± 2 °C under argon. Progress of the reaction was followed by TLC and GC. Conversions were calculated by GC, using *n*-nonane as an internal standard.

4.6. General procedure for recycling of the catalyst 7a

The catalyst **7a** (0.025 mmol, 2.5 mol%) was placed in a Schlenk tube. The tube was filled with argon and CH_2Cl_2 (40 mL) was added. To this a solution of the substrate **10b–d** (1.0 mmol) in CH_2Cl_2 (5 mL) was added. The resulting solution was stirred at 20 or 0 °C for 0.3–2 h. The solvent was evaporated and the residue was dissolved in minimal amount of CH_2Cl_2. The catalyst was precipitated with cold *n*-pentane. The crude **7a** was purified by column chromatography (0–20% ethyl acetate/*c*-hexane). The catalyst **7a** was obtained as a green solid. The product **11b–d** was formed in quantitative yield (purity >98% by GC).

4.7. Catalytic RCM of diene 12 with catalysts 1c, 1e, 7a and 7b

Diene **12** (7.5 mmol) was dissolved in degassed toluene (554 mL) and placed in a reaction flask under nitrogen. The solution was heated to 80 °C and the first portion of catalyst **1c**, **1e**, **7a** and **7b** (0.4 mol% Ru) was added to the stirred solution as a solid. After stirring at this temperature for 60 min. the second amount of the catalyst (0.2 mol% Ru) was added and the solution was stirred for another 60 min. Progress of the reaction was followed by HPLC.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.041.

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