

Article

Ruthenium Metathesis Catalysts with Imidazole Ligands

Peng Ma ¹, Jiaren Zhang ^{2,*}, Xiaqian Wu ¹ and Jianhui Wang ^{1,3,*}

¹ Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China

² PetroChina Petrochemical Research Institute, Beijing 102206, China

³ Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

* Correspondence: zhangjiaren@petrochina.com.cn (J.Z.); wjh@tju.edu.cn (J.W.)

Abstract: Phosphine-free ruthenium benzylidene complexes containing imidazole ligands are reported. These catalysts are effective for ring-closing metathesis (RCM) and cross-metathesis (CM) reactions at high temperatures, where the more widely used phosphine-containing *N*-heterocyclic carbene-based ruthenium catalysts show side reactions. This discovery opens up a pathway to develop more selective ruthenium metathesis catalysts for reactions requiring harsh conditions.

Keywords: ruthenium catalysts; olefin metathesis; imidazole ligands

1. Introduction

Olefin metathesis (OM), an essential method for the construction of carbon–carbon double bonds, has been used in many applications by introducing well-characterized ruthenium organometallic complexes [1–6]. In the case of ruthenium catalysts, introducing *N*-heterocyclic carbenes (NHCs) as ligands (Figure 1, Grubbs II, 2) led to a number of air- and moisture-stable catalysts compared to Grubbs I, which contains two Pcy₃ ligands (Figure 1, 1) [7–9]. In addition, the more specialized phosphine-free ruthenium complexes (containing one NHC ligand) such as nitrogen-ligated (Figure 1, Grubbs III, 3) [10] and oxygen-ligated (Figure 1, Hoveyda–Grubbs II, 4) [11] ruthenium catalysts have been introduced to allow for better results in industrially important metathesis reactions.



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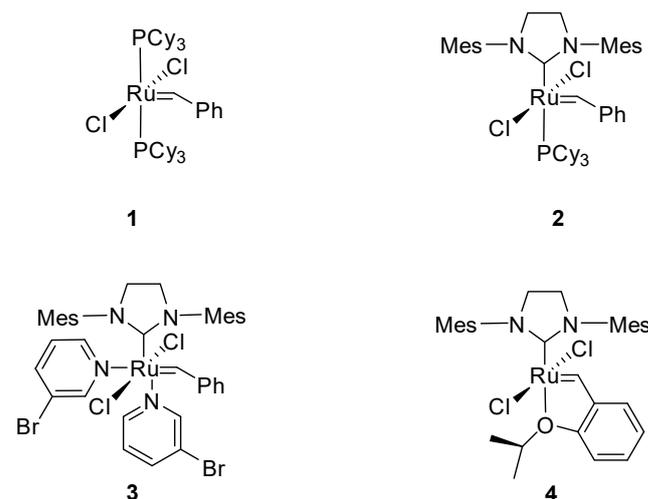
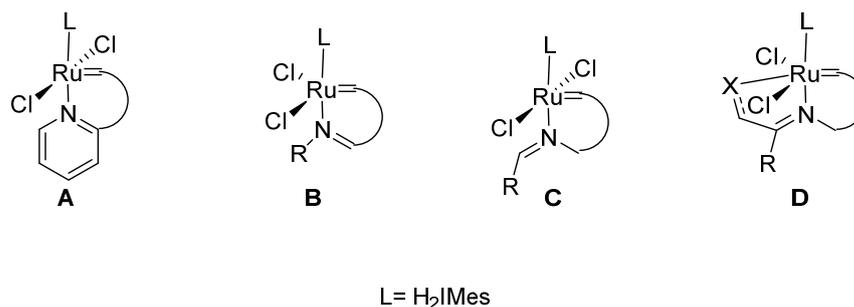


Figure 1. Ruthenium olefin metathesis catalysts 1–4.

Since Grubbs reported the first nitrogen-chelated ruthenium catalyst containing two pyridine ligands [12], a series of phosphine-free ruthenium catalysts containing a pyridine or imine ligand have been reported (Scheme 1) [13–38]. For example, Schrodli et al. [18] disclosed a Ru catalyst with motif A that showed higher catalytic activity in ring-opening olefin metathesis polymerization (ROMP). Grubbs' group [20] and Slugovc and Grela's

group [23] synthesized a series of nitrogen-chelated ruthenium complexes containing an imine ligand with motif B or C. Catalysts for multisite chelation were reported by our group in 2016, which exhibited high activity for the RCM and CM reactions (motif D) [24]. However, compared with the free nitrogen-chelated Ru catalysts, the endocyclic nitrogen-chelated model (Scheme 1, A–D) resulted in lower initiation rates due to the stronger binding of the Ru–N bond. In addition, Grubbs noted that the pyridine ligands in $[(\text{H}_2\text{IMes})(\text{pyridine})_2(\text{Cl})_2\text{Ru}=\text{CHPh}]$ can be readily replaced with phosphanes [12]. Given the similar nature of pyridine and imidazole [39], it seems logical to test whether the imidazole ligands, after transformation into the corresponding ruthenium complexes (Figure 1), act as OM catalysts and what the properties of this system will be.



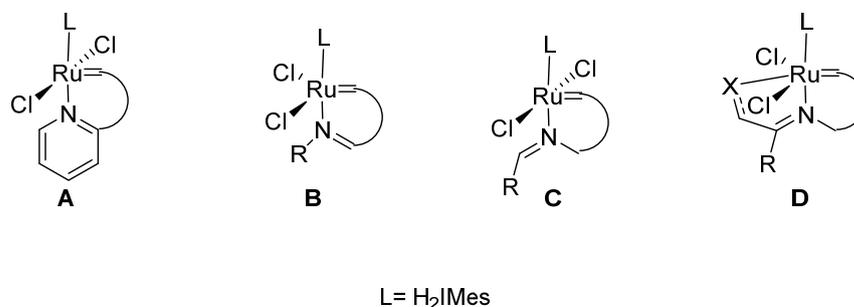
Scheme 1. Nitrogen-ligated ruthenium catalysts.

Here, we disclose a method for the stepwise preparation of a NHC ruthenium complex containing two imidazole ligands and demonstrate its high performance in RCM and CM reactions at high temperatures, as compared to the commercial phosphine-containing ruthenium catalysts, such as Grubbs II, that show side reactions [40]. To the best of our knowledge, the catalytic properties of the Grubbs catalysts bearing imidazole ligands have rarely been described in the related chemical literature. Only Schanz's group [41,42] and Öztürk and coworker [43] reported that using ruthenium benzylidene complexes containing 1-methylimidazole and poly(*N*-vinylimidazole) in combination with an excess of mineral acids (H_3PO_4 or HCl) to form 14 electron-active Ru complexes demonstrated its high performance in ROMP and CM reactions.

2. Results and Discussion

2.1. Synthesis of Catalysts 6a and 6b

Complexes **6a** and **6b** were then obtained in moderate to fair yields by using commercially available Ru precursor **2** in reaction with 1-mesityl-1H-imidazole **5a** or 1-benzyl-1H-imidazole **5b** (Scheme 2). All complexes were characterized via NMR spectroscopy and HRMS.



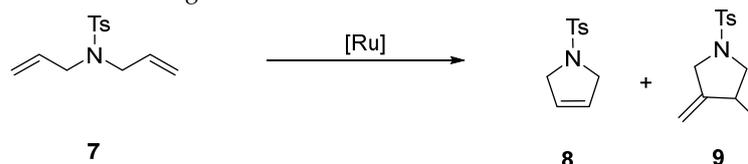
Scheme 2. Synthesis of **6a** and **6b**.

2.2. RCM Transformations

The catalytic behavior of Ru catalysts **6a–6b** was first evaluated in the model RCM reaction of *N,N*-diallyl-4-methylbenzenesulfonamide **7**, and the results are summarized

in Table 1. Since **6a–6b**, as expected, gave essentially the same selectivity while producing RCM product **8** and cycloisomerization product **9**, for a better understanding of the results, only the RCM reactions promoted by the Ru catalyst **6b** are reported in Table 1. For comparison, parallel RCM reactions performed with **2** were included in Table 1. Moreover, to put our results in a more general context, parallel reactions promoted by the Schanz catalyst (containing two 1-methylimidazoles and one NHC ligand) [42] in combination with mineral acids (H₃PO₄ or HCl) were also added.

Table 1. Screening of RCM reaction conditions ^a.



Entry	[Ru]	Temp (°C)	Time (h)	Additive	Solvent	Conv. (%)	Yield of 8	Yield of 9
1	2	25	4	-	DCM	>99	97	-
2	6b	25	4	-	DCM	31	13	15
3 ^b	6b	25	12	HCl	DCM	>99	9	86
4 ^b	6b	25	12	H ₃ PO ₄	DCM	>99	40	56
5 ^b	Schanz	25	12	HCl	DCM	>99	Trace	92
6 ^b	Schanz	25	12	H ₃ PO ₄	DCM	96	80	11
7	6b	40	4	-	DCM	45	21	23
8	6b	60	4	-	Toluene	61	26	31
9	6b	70	4	-	Toluene	73	33	38
10	6b	80	4	-	Toluene	>99	43	52
11	6b	80	4	phenylacetylene	Toluene	91	14	73
12	6b	80	4	3-bromoprop-1-yne	Toluene	39	36	-
13	6b	80	12	3-bromoprop-1-yne	Toluene	>99	95	-
14	6b	80	8	3-bromoprop-1-yne	Toluene	70	66	-
15 ^c	6b	80	12	3-bromoprop-1-yne	Toluene	95	89	-
16 ^d	6b	80	12	3-bromoprop-1-yne	Toluene	>99	95	-
17	6b	110	12	3-bromoprop-1-yne	Toluene	79	70	-

^a Substrate (0.5 mmol), solvent (0.5 mL), [Ru] (1 mol%), and additive (3 mol%). The reaction was carried out at 80 °C. ^b Additive (30 mol%). ^c Additive (2 mol%). ^d Additive (5 mol%).

The RCM reaction of *N*-protecting diene **7** with catalyst **2** proceeded almost quantitatively at 25 °C, and no isomerization product **9** was observed (Table 1, entry 1). Regardless of the poor efficiency displayed by Ru catalyst **6b** in the same reaction (entry 2), we thought to investigate the factors affecting its catalytic behavior in the RCM reactions. Note that the formation of isomerization product **9** may be ascribed to the oxidative coupling of the diene to the Ru center followed by β -elimination and reductive elimination when the Ru complex in RCM reactions displayed a latent catalytic property [44,45]. Schanz disclosed that the coordination of imidazole ligand precursors to Grubbs-type catalysts generated a latent catalytic system, which could translate into an active Ru complex through the addition of mineral acids (H₃PO₄ or HCl) [41,42]. Encouraged by this result, we tried to use H₃PO₄ or HCl as an additive to enhance the activity and chemoselectivity of **6b**. Additionally, the results revealed that **6b** did not have a significant enhancement in the yield of **8** along with the formation of **9**, but the Schanz catalyst gave a better result in the presence of H₃PO₄ (entries 3–6). Screening mineral acids as an additive did not give a better result; therefore, we turned our attention to the reaction temperature. As the temperature increased, the yield of product **8** also increased; however, it also did not suppress the formation of isomerization product **9** (entries 7–10). Importantly, when the RCM reaction of *N*-protecting diene **7** was carried out in toluene at 80 °C by using **6b** as a catalyst, the conversion of **7** was more than 99% (entry 10). Moreover, Demonceau [44] and Dixneuf [45] reported that using terminal alkynes as additives could inhibit the isomerization product by promoting the formation of an active Ru complex. These results encouraged us to continue screening different terminal alkynes as additives at this temperature. The use of 3 mol% of phenylacetylene as an additive led to a slight decrease in the yield of **8**, along with a considerable increase in the formation of **9** (entry 11). Using 3-bromoprop-1-yne as

an additive did not cause a significant enhancement in the yield of product **8**, but inhibited the formation of **9** (entry 12). Interestingly, a prolonged reaction time (from 4 h to 12 h) gave RCM product **8** a 95% yield by using 3 mol% of 3-bromoprop-1-yne as an additive, and the formation of **9** was not observed (entry 13). Changing the reaction temperature, reaction time, and the amount of additive did not lead to a definite improvement in the yield of **8** (entries 14–17).

Having the optimal parameters in hand, we opted to test the activity of **6a** and **6b** in a set of RCM reactions (Table 2). In general, **6b** was found to smoothly realize the ring closure of tested substrates **7**, **9**, **11**, **13**, **17**, and **19**, giving corresponding five-, six-, or seven-membered cyclic olefins in a higher yield with respect to **6a**. However, for eneyne substrate **15**, neither catalyst **6a** nor **6b** could promote the RCM reaction.

Table 2. Substrate scope of RCM reactions ^a.

Entry	Substrate	Product	[Ru]	Yield
1			6a	93
			6b	95
2			6a	85
			6b	89
3			6a	82
			6b	88
4			6a	86
			6b	89
5			6a	0
			6b	0
6			6a	82
			6b	87
7			6a	80
			6b	86

^a Substrate (0.5 mmol), toluene (0.5 mL), [Ru] (1 mol%), and 3-bromoprop-1-yne (3 mol%) at 80 °C for 12 h. Isolate yield.

The catalytic profile of **6b** was then evaluated in the CM reactions of two different terminal olefins without an additive. Moreover, to ensure the fairness of the test, parallel reactions catalyzed by **2** and the Schanz catalyst were also added (Figure 2). Although **2** showed slightly higher reactivity, styrenes with R¹ as a 4-F, 4-Me, or 4-MeO moiety were all reacted with (allyloxy)benzene to give CM products **23–25** by using **6b** in an additive-free manner. Out of curiosity, the CM reaction of styrene and (allyloxy)benzene was also carried out at 80 °C, giving **25** in a 90% yield, which exhibited the ability of **6b** to work under harsh conditions. Catalyst **6b** was also entered into a reaction of styrene and terminal olefins with various functional groups (-CN and -COOMe; **26–27**), but catalyst **2** also had a superior conversion. Moreover, the Schanz catalyst was used to synthesize **23–27** in an additive-free manner, and the results showed that **6b** and the Schanz catalyst perform similar activities in the CM reactions.

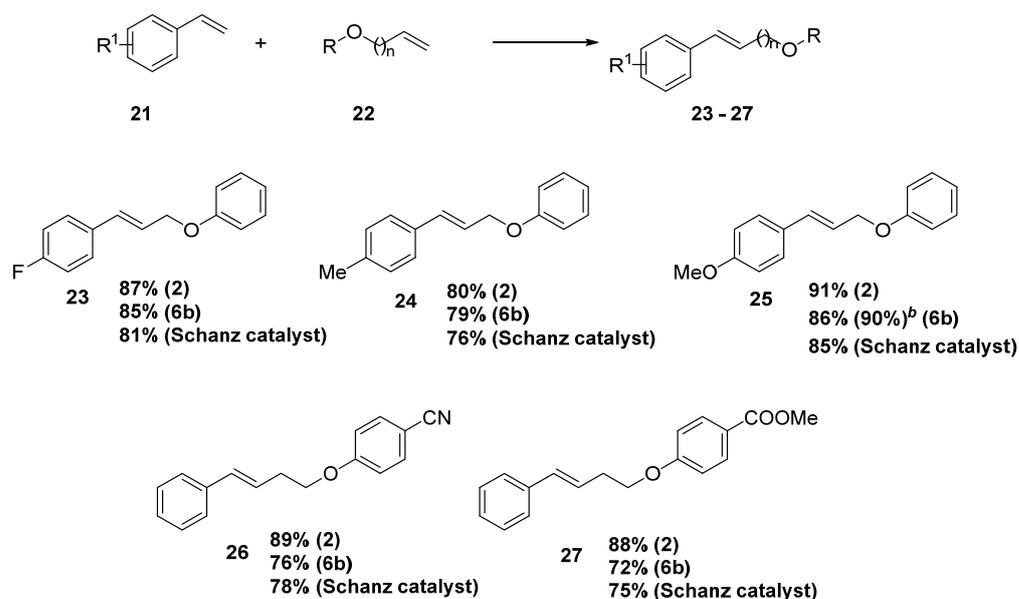


Figure 2. Substrate scope of CM reactions. Substrate **21** (5.0 mmol), substrate **22** (0.5 mmol), DCM (0.5 mL), and [Ru] (2.5 mol%) at 40 °C for 12 h. Isolate yield. ^b Toluene as solvent at 80 °C for 12 h.

3. Materials and Methods

3.1. Instruments and Reagents

1-Benzyl-1H-imidazole **5b** and most alkenes were acquired from commercial suppliers and were used without further purification. Here, 1-mesityl-1H-imidazole **5a** was synthesized according to published procedures [46]. The ¹H and ¹³C NMR spectra were obtained at 25 °C in CDCl₃ on a Bruker AV 400 NMR spectrometer (Bruker Co., Faellanden, Switzerland), in which the chemical shifts (δ in ppm) were established with respect to CHCl₃. High-resolution mass spectrometry (HRMS) was performed on a Bruker microTOF-QII instrument (Bruker Daltonik GmbH, Bremen, Germany).

3.2. Catalytic Tests

3.2.1. RCM Reactions

To the solution of N-protecting diene (0.5 mmol) and an additive (3 mol%) in a dry solvent (DCM, or toluene, 0.5 mL), 1.0 mol% of a corresponding catalyst (**2**, **6a**, **6b**, or the Schanz catalyst) was added in one portion in N₂. The resulting mixture was stirred under the given conditions (see Tables 1 and 2) for 12 h. After the reaction time was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO₂, eluent: from n-hexane to 10% EtOAc/n-hexane).

3.2.2. CM Reactions

To the solution of styrene (5.0 mmol) and O-protecting terminal olefins (0.5 mmol) in a dry solvent (DCM or toluene, 0.5 mL), 2.5 mol% of a corresponding catalyst (**2**, **6b**, or the Schanz catalyst) was added in one portion in N₂. The resulting mixture was stirred under the given conditions (see Figure 2) for 12 h. After the reaction time was completed, all volatiles were removed under reduced pressure and the crude product was purified using column chromatography (SiO₂, eluent: from n-hexane to 10% EtOAc/n-hexane).

4. Conclusions

Two imidazole ruthenium catalysts were synthesized for the first time. The high activity of the synthesized ruthenium precatalysts, containing *N*-Mes or *N*-Bn imidazole ligands, makes them very good precatalysts for high-temperature RCM and CM reactions. Maintaining of the high catalytic activity of the ruthenium precatalysts under harsh conditions may be attributed to the strengthening of the Ru-N bond.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13020276/s1>, Figure S1–S34: ^1H and ^{13}C NMR spectra of **5a**, **6a**, **6b**, **8**, **10**, **12**, **14**, **18**, **20**, **23–27**.

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Data Availability Statement: Data are contained within the article or the Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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