An Easily Assembled Highly Active Ruthenium Initiator for Olefin Metathesis

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Abstract: A practical and easily assembled synthesis of new ruthenium alkylidene precatalyst **8** is described, which exhibits excellent metathesis activity in ring-closing and ring-opening cross metathesis processes.

Key words: catalysis, metathesis, ring-closing, ring-opening, ruthenium

Since olefin metathesis has emerged as a powerful tool for carbon-carbon bond formation,[1] much effort has been devoted to the development of new efficient and practical olefin metathesis catalysts. It is in this context that ruthenium complexes, bearing N-heterocyclic carbene (NHC) ligands such as **1**[2] have attracted much attention, due to their high activity and remarkable air/water stability. The introduction of a phosphine-free variant incorporating a chelating *o*-isopropoxybenzylidene ligand (catalyst **2**) has enabled catalyst recovery by column chromatography.[3] This catalyst possesses improved general reactivity towards electron deficient alkenes[4] and is readily amenable to immobilizations.[5] We have found that the superior stability of **2** comes hand in hand with longer reaction times. Our investigations aimed at the preparation of highly active and stable ruthenium-initiators recently led to the discovery of a variant **3** which possesses similar shelf-stability but a remarkable activity that surpasses that of **2** and even **1** (Figure 1).[6]

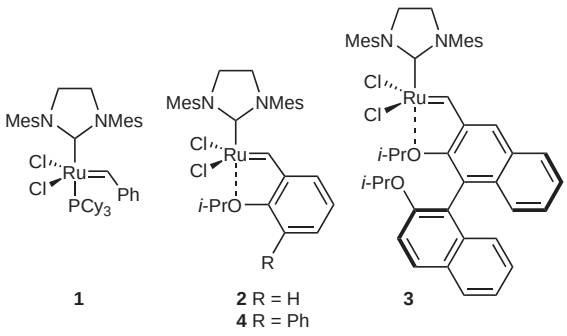
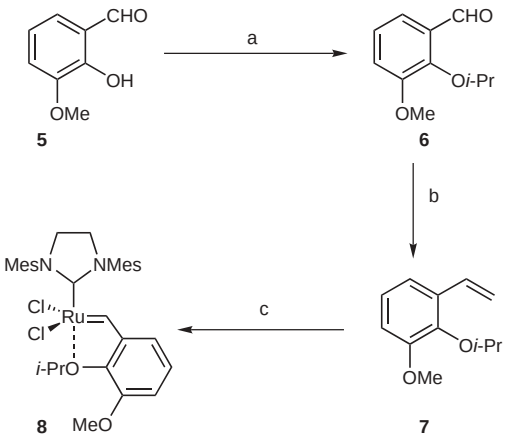


Figure 1 Ruthenium precatalysts.

This enhanced reactivity prompted us to undertake a more systematic study on the effect of the substituent R on the *o*-isopropoxybenzylidene moiety. Apparently steric effects of R in **4** seemed to be responsible for its improved reactivity. Given the substitution pattern of **4** we set out to investigate the introduction of less elaborate substituents R on the benzylidene moiety that could also lead to catalysts with enhanced activity, without requiring expensive and multistep syntheses, which would detract from catalyst utility. However the synthesis of corresponding analogues of **2** with either a methyl or a second alkyl moiety as R proved to be non-trivial. These results indicate that the presence of steric bulk adjacent to the isopropoxy group also seems to be critical and therefore not every desired substituent in the catalyst is accessible. We then set out to synthesize complex **8**, a 3-methoxy analogue of **2**. The alkoxy functionality is of particular interest because it represents a functional handle with regard to immobilization.

Herein we report the synthesis of **8** and its activity in ring-closing metathesis (RCM) and ring-opening cross metathesis (ROM-CM).

2-Isopropoxy-3-methoxybezaldehyde (**6**) was synthesized from commercially available *o*-vanillin (**5**) through alkylation using sodium hydride and isopropyl bromide in DMF. Subsequent Wittig olefination delivered styrene **7**. The bright green ruthenium complex **8** was prepared by the reaction of **1** with two equivalents of **7** in the presence of CuCl as a phosphane scavenger in CH_2Cl_2, and was isolated by flash chromatography (FC) on silica gel (Scheme 1).[7] Precatalyst **8** has a comparable air/moisture stability to **2**.



Scheme 1 *Reagents and conditions* a) **5** (1.0 Equiv), NaH (1.2 equiv), DMF (0.5 M), 0 °C to r.t., then *i*-PrBr (1.5 equiv), 50 °C, 36 h, 67%; b) *t*-BuOK (2.0 equiv), Ph_3PCH_3Br (2.0 equiv), Et_2O (0.1 M), 0 °C, 10 min, then **6** (1.0 equiv), 5 min, 98%; c) **1** (1.0 equiv), **7** (2.0 equiv), CuCl (1.1 equiv), CH_2Cl_2 (0.01 M), 40 °C, 1 h, 81%.

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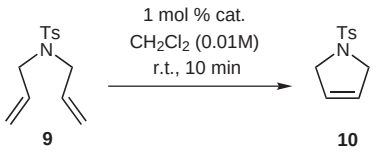
The potential of **8** was first tested in the RCM of tosylamide **9** (Scheme 2).[8] To our delight, in a matter of minutes complete conversion of **9** was observed in CH_2Cl_2 at room temperature, using as little as 1 mol% of **8**. The activity of complex **8** in this reaction was therefore significantly higher than that of **2** and **1** under identical reaction conditions.[6a]

Ranges of substrates were then examined, encompassing various functional groups and ring sizes and the results are presented in Table 1. All reactions were carried out at room temperature in CH_2Cl_2 (0.05 M) under an inert atmosphere in the presence of 0.1–0.5 mol% of the pre-catalysts **1** and **8**. After 10–20 minutes, the reaction mixtures were quenched by using ethyl vinyl ether.



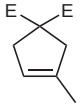
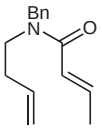
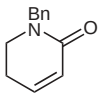
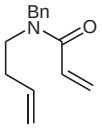
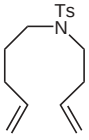
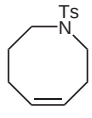
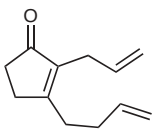
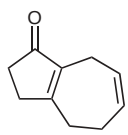
cat.	yield [%]
1	44
2	13
4	>99
8	98

Scheme 2 RCM of **9** using **1**, **2** and **8**.

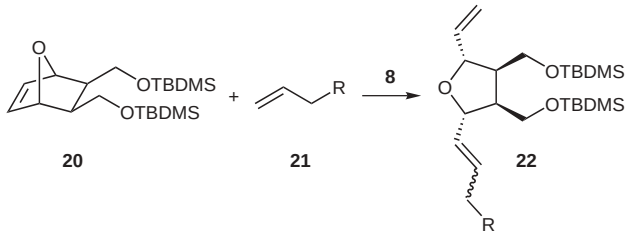
An enhanced activity of **8**, compared to **1** is obvious from an examination of the results. For example, the RCM of **16** to **17** (Table 1, entry 8) proceeded smoothly using 0.5 mol% of **8** with an isolated yield of 74% after 10 minutes. In contrast only 8% of **17** (Table 1, entry 7) could be detected by HPLC when the same reaction was promoted by **1** under identical conditions. Another conspicuous example is the conversion of **13** to dihydropyridinone **14** in 93% yield (Table 1, entry 4) after FC and 20 minutes reaction time using only 0.1 mol% of **8**, whereas under identical conditions **1** gave only 5% conversion (Table 1, entry 3) detected by HPLC analysis. Interestingly, terminal acrylamide **15** proved to be less reactive. We propose that the formation of a more stable ethylidene propagating species from substrate **13** accounts for its fast conversion to **14**. However it must be noted that similar yields were achieved in RCM reactions by using catalyst **1** and increased reaction times (up to 14 h).

In addition, the application of **8** in ROM-CM processes was also tested (Scheme 3).[9] Oxanorbornene derivative **20** was ring-opened in the presence of 2 equivalents of various functionalized alkenes of general type **21** at room temperature.

Table 1 RCM Using **1**, **4** and **8**

Entry	Substrate	Product	Catatlyst (mol%)	Time (min)	Yield (%)
1[d]			**1** (0.5)	20	43[b]
2[d]			**4** (0.5)	10	99[b]
			8 (0.5)	20	85[b]
	11	**12**			
3			**1** (0.1)	20	5[c]
4			**8** (0.1)	20	93[a]
	13	**14**			
5		**14**	**1** (0.1)	20	1[c]
6			**8** (0.1)	20	24[c]
	15				
7			**1** (0.5)	10	8[c]
8			**8** (0.5)	10	74[a]
	16	**17**			
9			**1** (0.5)	20	24[a]
10			**8** (0.5)	20	88[a]
	18	**19**			

[a] Isolated yields after column chromatography.
[b] Conversions were determined by ^{1}H NMR spectroscopy.
[c] Conversions were determined by HPLC.
[d] E = CO_2Et.



Scheme 3 ROM-CM using catalyst **8**.

Allyl trimethylsilane **21a** proved to be the best substrate for the ROM-CM processes (Table 2). After only 5 minutes using 0.05 mol% of **8** nearly quantitative conversion was observed by ^{1}H NMR spectroscopy. In general, low amounts of catalyst were required for these processes and a high functional group tolerance could be demonstrated. Even sulfide **21d** reacted, although higher catalyst loadings and longer reaction times were required.[10]

In summary, we have developed a practical and in particular easily accessible precatalyst **8**, which exhibits excellent metathesis activity, surpassing that of **1** and **2**. Reactions with **8** are slightly slower in comparison to those with **4** (for example, see formation of **10** and **12**). However, **8** is easier to prepare and has a better shelf stability which is important for practical purposes. *o*-Substitution next to the isopropoxy group is effective for high activity up to the present our work, however, its detail is not clear yet.[11] The same effect has recently been used successfully by Hoveyda et al.[12] In addition to an *ortho*-effect, electronic effects can influence the reactivity of styrene ether complexes. Studies in this field have been published by Grela,[13] Hoveyda[12] and by us.[14] On the other hand, development of highly active immobilized catalyst will be realized by the present work. Further developments of homogeneous and heterogeneous ruthenium metathesis initiator having excellent activity and stability are in progress in our laboratory.

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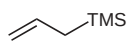
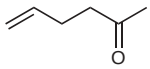
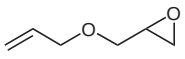
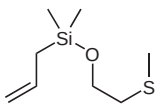
(7) **Procedure for the Preparation of Catalyst 8:** To a solution of **7** (136 mg, 0.71 mmol) in CH_2Cl_2 (35 mL) was added CuCl (38 mg, 0.39 mmol) and **1** (300 mg, 0.35 mmol) under an atmosphere of N_2. The reaction mixture was stirred for 1 h at 40 °C, concentrated, dissolved in a minimal volume of CH_2Cl_2 and passed through a Pasteur pipette containing a plug of cotton, and then concentrated. The residue was

Table 2 ROM-CM Results

Entry	CM-substrate (CH_2=$CHCH_2R$)	Product	Catalyst (mol%)	Time (min)	Yield (%)
1	 **21**	**22a**	**8** (0.05)	5	98[a] 83[b]
2	 **21b**	**22b**	**8** (0.5)	5	99[a] 72[b]
3	 **21c**	**22c**	**8** (0.5)	5	99[a] 51[b]
4	 **21d**	**22d**	**8** (3)[c]	14 h	86[a] 70[b]

[a] Conversions were determined by ^{1}H NMR spectroscopy.
[b] Isolated yields after column chromatography.
[c] Reaction was carried out at reflux.

purified by column chromatography on silica gel (hexane/MTBE 2:1) to give **8** (188 mg, 81%) as a green solid. IR (ATR): ν = 3482 (w), 2971 (s), 2918 (s), 1701 (m), 1607 (w), 1574 (s), 1475 (s), 1445 (s), 1267 (ss), 1106 (s), 852 (w), 759 (w) cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2): δ = 1.15 [d, *J* = 6 Hz, 6 H, $OCH(CH_3)_2$], 2.40 (br s, 18 H, CH_3-Mes), 3.78 (s, 3 H, OCH_3), 4.14 (s, 4 H, H-2), 5.69 [qsep, *J* = 6, 6 Hz, 1 H, $OCH(CH_3)_2$], 6.54 (d, *J* = 8 Hz, 1 H, CH-Ar), 6.88 (dd, *J* = 8, 8 Hz, 1 H, CH-Ar), 7.06 (br s, 4 H, CH-Mes), 7.15 (d, *J* = 8 Hz, 1 H, CH-Ar), 16.51 (s, 1 H, H-3). ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 18.4 (CH_3, Mes), 20.2 (CH_3, Mes), 20.9 [CH_3, $OCH(CH_3)_2$], 21.6 [CH_3, $OCH(CH_3)_2$], 51.5 (br, CH_2, C-2), 56.3 (CH_3, OCH_3), 80.5 [CH, $OCH(CH_3)_2$], 114.1 (CH, Ar), 115.4 (CH, Ar), 123.4 (CH, Ar), 129.2 (br, CH, Mes), 138.8 (Cq), 138.9 (Cq), 139.7 (Cq), 139.9 (Cq), 147.6 (Cq), 149.6 (Cq), 210.6 (Cq, C-2), 297.6 (CH, C-3). LRMS (FAB): *m/z* (%) = 656 (2) [M^+], 578 (6), 541 (2), 441 (5), 405 (34) 307 (37), 147 (22), 109 (23), 91 (42), 69 (78), 55 (100). Anal. Calcd for $C_{32}H_{40}N_2O_2Cl_2Ru$: C, 58.53; H, 6.14; N, 4.27. Found: C, 58.18; H, 5.90; N, 4.51.

(8) **General Procedure for RCM:** The acyclic **11**, **13**, **15**, **16**, **18** diene was dissolved in dry CH_2Cl_2 (0.05 M) at r.t., **8** (0.1–0.5 mol%) was added and the solution was stirred for 10–20 min at r.t. Subsequently the reaction mixture was quenched using freshly distilled ethyl vinyl ether and concentrated. The crude product was purified by FC on silica gel (hexane/EE or hexane/MTBE), respectively.

(9) **General Procedure for ROM-CM**: The Oxanorbornene derivative **20** was dissolved in dry CH_2Cl_2 (0.05 M) at r.t., 2 equiv of the desired cross metathesis partner **21a–d** and **8** (0.05–3.00 mol%) were added and the solution was stirred for 5 min at r.t. (**21d**: 14 h at reflux). Subsequently, the reaction mixture was quenched using freshly distilled ethyl vinyl ether and concentrated. The crude product **22a–d**[15] was purified by FC on silica gel (hexane/EE or hexane/MTBE).

(10) For an example of RCM using sulfide substrates see: Spagnol, G.; Heck, M.-P.; Nolan, S. P.; Mioskowski, C. *Org. Lett.* **2002**, *4*, 1767.

(11) (a) For example, the catalyst, which is substituted in alkyl group instead of methoxy group, could not be isolated: Zaja, M.; Blechert, S. unpublished results. (b) Mechanism of phosphine based ruthenium metathesis catalysts, see: Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749. (c) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543. (d) Love, J. A.; Sanford, M. S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 10103.

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(15) Selected spectroscopic data:
Compound **22b**: IR (ATR): ν = 2954 (s), 2928 (s), 2857 (s), 1720 (s), 1643 (w), 1472 (m), 1255 (s), 1089 (s), 836 (ss) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, *E*/*Z* = 1:1): δ = 0.02–0.06 [m, H, $OSi(CH_3)_2$], 0.88 [m, 18 H, $OSiC(CH_3)_3$], 2.11–2.54 (m, 8 H, H-4, H-, H-9, H-10 and H-12), 3.62–3.77 (m, 2 H, H-13 and H-14), 4.19 (dd, *J* = 7, 7 Hz, 0.5 H, H-6), 4.26 (m, 1 H, H-3), 4.61 (dd, *J* = 7 Hz, 0.5 H, H-6), 5.09 (br dd, *J* = 10, 5 Hz, 1 H, H-1, *Z*), 5.23 (d, *J* = 17 Hz, 1 H, H-1, *E*), 5.42–5.53 (m, 1.5 H, H-7 and H-8), 5.65 (dt, *J* = 15, 7 Hz, 0.5 H, H-8, *E*), 5.86 (m, 1 H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = –5.6, –5.6, –5.5 [CH_3, $OSi(CH_3)_2$], 18.1, 18.1 [C_q, $OSiC(CH_3)_3$], 21.9 (CH_2), 25.8 [CH_3, $OSiC(CH_3)_3$], 26.3 (CH_2), 29.9, 29.9 (CH, C-12), 43.0, 43.5, (CH_2), 48.9, 49.0, 49.1, 49.8 (CH, C-4 and C-5), 60.5, 60.6, 60.8, 60.9 (CH_2, C-13 and C-14), 76.3, 81.8, 82.2, 82.3 (CH, C-3 and C-6), 115.3, 115.5 (CH_2, C-1), 131.0, 131.0, 131.8, 131.9 (CH, C-7 and C-8), 139.4, 139.6 (CH, C-2). LRMS (EI): *m/z* (%) = 482 (<1) [M^+], 425 (42), 189 (31), 147 (67), 89 (67), 73 (100). HRMS: *m/z* calcd for $C_{26}H_{50}O_4Si_2$ [M^+]: 482.3248; found: 482.3259. Anal. Calcd for $C_{26}H_{50}O_3Si_2$: C, 64.67; H, 10.44. Found: C, 64.63; H, 10.21.
Compound **22c**: IR (ATR): ν = 2954 (s), 2929 (s), 2857 (s), 1644 (w), 1255 (s), 1090 (s), 837 (ss) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, two diastereomers 1:1, *E*/*Z* = 4:1): δ = 0.04 [br s, 12 H, $OSi(CH_3)_2$], 0.88 [br s, 18 H, $OSiC(CH_3)_3$], 2.14–2.23 (m, 2 H), 2.59–2.63 (m, 1 H), 2.79 (dt, *J* = 4, 4 Hz, 1 H), 3.14 (m, 1 H), 3.34–3.45 (m, 1 H), 3.63–3.85 (m, 5 H), 3.99–4.49 (m, 3 H), 4.59 (br t, *J* = 6 Hz, 1 H), 5.07 (br d, *J* = 10 Hz, 0.2 H), 5.11 (dd, *J* = 10, 4 Hz, 0.8 H), 5.22 (br d, *J* = 17 Hz, 0.2 H), 5.24 (br d, *J* = 17 Hz, 0.8 H), 5.54–5.79 (m, 2 H), 5.84 (m, 1 H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = –5.6, –5.5, –5.5, –5.5, [CH_3, $OSi(CH_3)_2$], 18.1, 18.2 [C_q, $OSiC(CH_3)_2$], 25.8, 25.8, 25.9, 26.0 [CH_3, $OSiC(CH_3)_2$], 44.3, 44.4, 44.4 (CH_2, C-12), 48.9, 49.0, 49.1, 49.7, 49.9, 50.6, 50.7, 50.8 (CH, C-4, C-5 and C-11), 60.2, 60.6, 60.7, 60.7, 60.8, 61.0, 61.1, 61.3 (CH_2, C-13 and C-14), 67.0, 67.1, 70.6, 70.6, 70.8, 71.3, 71.3, 71.4 (CH_2, C-9 and C-10), 76.1, 76.7, 81.1, 81.3, 81. 7, 82.3, 82.4, 82.7(CH, C-3 and C-6), 115.0, 115.5, 115.7 (CH_2, C-1), 127.5, 127.5,128.6, 128.7, 133.8, 133.9, 134.4, 134.4 (CH, C-7 and C-8), 139.2, 139.4, 139.7 (CH, C-2). LRMS (EI): *m/z* (%) = 455 (8) [M^+ – (*tert*-Bu)], 189 (20), 147 (48), 131 (100), 89 (84), 73 (95). HRMS: *m/z* calcd for $C_{23}H_{43}O_5Si_2$ [M^+ – (*tert*-Bu)]: 455.2649; found: 455.2651. Anal. Calcd for $C_{27}H_{52}O_5Si_2$: C, 63.23; H, 10.22. Found: C, 63.10; H, 9.86.
Compound **22d**: IR (ATR): ν = 2954 (s), 2928 (s), 2857 (s), 1644 (w), 1472 (m), 1252 (s), 1087 (s), 836 (ss) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, *E*/*Z* = 1/1): δ = 0.03 [s, 3 H, $OSi(CH_3)_2$], 0.04 [s, 3 H, $OSi(CH_3)_2$], 0.04 [s, 3 H, $OSi(CH_3)_2$], 0.05 [s, 3 H, $OSi(CH_3)_2$], 0.12 (s, 3 H, H-10), 0.14 (s, 1.5 H, H-10), 0.15 (s, 1.5 H, H-10), 0.89 [s, 9 H, $OSiC(CH_3)_3$], 0.90 [s, 4.5 H, $OSiC(CH_3)_3$], 0.90 [s, 4.5 H, $OSiC(CH_3)_3$], 1.58–1.66 (m, 1.5 H, H-9), 1.73 (dd, *J* = 9, 2 Hz, 0.5 H, H-9), 2.09–2.23 (m, 5 H, H-4, H-5 and H-13), 2.62 (t, *J* = 7 Hz, 2 H, H-12), 3.63–3.80 (m, 6 H, H-11, H-14 and H-15), 4.19 (t, *J* = 8 Hz, 0.5 H, H-6), 4.27 (dt, *J* = 6, 7 Hz, 1 H, H-3), (dd, *J* = 8, 7 Hz, 0.5 H, H-6), 5.08 (dd, *J* = 10, 4 Hz, 1 H, H-1, *Z*), 5.23 (ddt, *J* = 17, 8, 2 Hz, 1 H, H-1, *E*), 5.34–5.41 (m, 1 H, H-7), 5.56 (dt, *J* = 10, 9 Hz, 0.5 H, H-8, *Z*), (dt, *J* = 16, 8 Hz, 0.5 H, H-8, *E*), 5.87 (dddd, *J* = 17, 10, 6, 2 Hz, 1 H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = –5.5, –5.5, –5.5 [CH_3, $OSi(CH_3)_2$], –2.4, –2.4, 2.3, 2.3 (CH_3, C-10), 16.1, 16.1 (CH_3, C-13), 18.1, 18.2 [C_q, $OSiC(CH_3)_3$], 18.9, 22.4 (CH_2, C-9), 25.8, 25.9, 25.9 [CH_3, $OSiC(CH_3)_3$], 36.3, 36.3 (CH_2, C-12), 49.0, 49.0, 49.1, 50.1 (CH, C-4 and C-5), 60.5, 60.6, 60.9, 61.0 (C-14 and C-15), 62.4, 62.4 (CH_2, C-11), 76.3, 82.0, 82.0, 82.1 (CH, C-3 and C-6), 115.1, 115.2 (CH_2, C-1), 127.7, 128.2 (CH, C-8), 129.7, 130.6 (CH, C-7), 139.7, 139.9 (CH, C-2). LRMS (EI): *m/z* (%) = 574 (<1) [M^+], 223 (3), 189 (4), 149 (100), 133 (6), 89(8), 75 (23). HRMS: *m/z* calcd for $C_{28}H_{58}O_4SSi_3$ [M^+]: 574.3364; found: 574.3371.