Polyhedron 76 (2014) 51–54

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, structure and catalytic study of oxygen chelated ruthenium (II) carbene complex

Guiyan Liu [a,*], Mingbo Shao [b], Huizhu Zhang [a], Jianhui Wang [b,*]

[a] College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry (Tianjin Normal University), Ministry of Education, Tianjin Normal University, Tianjin 300387, PR China
[b] Department of Chemistry, College of Science, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:
Received 23 January 2014
Accepted 20 March 2014
Available online 1 April 2014

Keywords:
Ruthenium (II)
N-heterocyclic carbene
Crystal structure
Coordination
Homogeneous catalysis

ABSTRACT

New oxygen chelated ruthenium carbene complex containing carbonyl oxygen and ether oxygen has been developed. The X-ray structure of the complex showed that the carbonyl oxygen of the amide and the terminal oxygen of the benzylidene ether are both coordinated to the metal to give an octahedral structure. The catalytic activities of this new complex for olefin metathesis reactions were investigated and it exhibited excellent performances for the ring-closing metathesis (RCM) of diethyl diallymalonate at 30 °C and even at 0 °C. The initiation rate of the catalyst was higher than that for the Hoveyda catalyst ($(H_2IMes)(Cl)_2Ru = C(H)(C_6H_4\text{-}2\text{-}OiPr)$) and it was also active for cross metathesis (CM).

1. Introduction

Owing to the advent of highly efficient, well-defined ruthenium catalysts **1**–**4** (Chart 1) [1], olefin metathesis has emerged as a powerful tool for constructing carbon–carbon double bonds [2]. Among these complexes, ruthenium-benzylidene catalyst **4** which introduced by Hoveyda and coworker bears N-heterocyclic carbene (NHC) ligand, and exhibits extraordinary activity and stability [1c]. However, compared with Grubbs catalyst **2**, it has a slowly initiate due to the donation of an electron from iPrO to ruthenium cause. The rate of initiation of chelated complexes is affected by the electronic and steric effects that act upon the Ru···O coordination. So, in order to boost the activity of **4**, all kinds of changes were done by researchers [3–7]. For example, in 2006, Bieniek et al. [6d] synthesized complex **5** by functionalizing the aliphatic end groups of the complexes by attaching an ester group which enhanced the leaving group properties of the styrenyl ether and in 2011 Bieniek et al. [6e] synthesized a series of complexes **6** with different substituents (an ester group, a ketonic group, or a malonic group). All of these complexes had an additional functional group the coordinated to the metal center. All these catalysts were found to exhibit higher activities than that of the unmodified complex **4** in ring-closing metathesis (RCM) and cross metathesis (CM) reactions for both standard and challenging substrates. On the basis of these researches; we herein report a new NHC ruthenium (II) complex in which the leaving group properties of the styrenyl ether of complex **4** is enhanced by attaching an amide functional group to the aliphatic end group. The carbonyl oxygen of the amide and the terminal oxygen of the benzylidene ether are both coordinated to the metal. In addition to structural study the catalytic activity of the new complex is explored.

2. Results and discussion

The synthesis of new complex is depicted in Scheme 1. Ester-substituted styrenyl ether **8** was prepared by reacting commercially available **7** with 2-bromo-propionic acid ethyl ester in the presence of potassium carbonate. The N,N-dimethyl substituted carbene ligand amide precursors **9** were obtained by hydrolysis and acylation of **8**. The precursor **9** was then reacted with **2** in the presence of copper (I) chloride in CH_2Cl_2 at 40 °C, as described by Kingsbury and co-workers. [1c]. This resulted in the exchange of the styrene group to give the desired catalyst **10** in good yield 65.7% as greenish crystalline solids.

Crystals of the new Ru complex **10** was grown by slow evaporation from CH_2Cl_2/ethyl acetate. The molecular structure of the complex is shown in Fig. 1, along with a selection of interatomic distances and bond angles. The X-ray structure shows that the arrangements of the ligands around the metal center have characteristics in common with those found in the Grubbs/Hoveyda

---

* Corresponding authors. Tel.: +86 13642014012; fax: +86 022 23766530 (G. Liu). Fax: +86 022 27403475 (J. Wang).

E-mail addresses: guiyanliu2013@163.com (G. Liu), wjh@tju.edu.cn (J. Wang).

http://dx.doi.org/10.1016/j.poly.2014.03.034

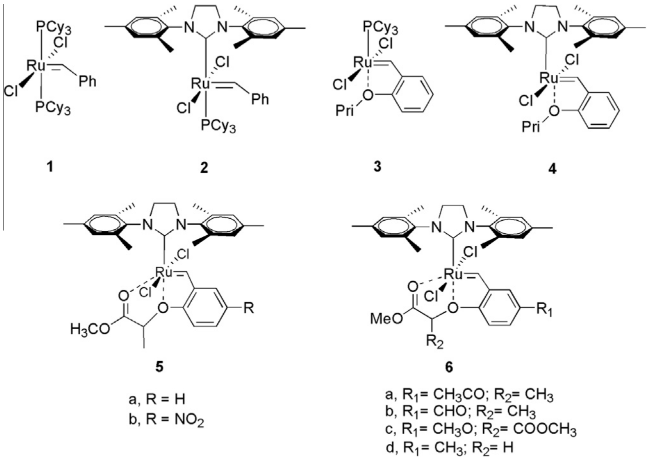
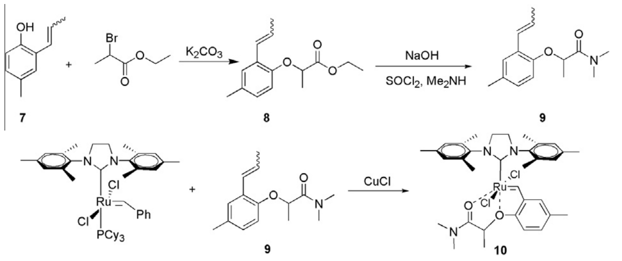


Chart 1. Ruthenium metathesis catalysts.



Scheme 1. Synthesis of oxygen chelated ruthenium (II) carbonyl complex **10**.

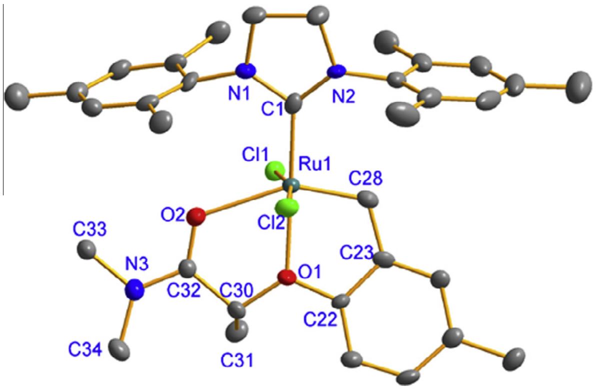


Fig. 1. Perspective view of the catalyst **10**. Ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and bond angles (deg): Ru(1)–C(1) = 1.972(5), Ru(1)–C(28) = 1.844(5), Ru(1)–O(1) = 2.171(3), Ru(1)–O(2) = 2.355(3), Ru(1)–Cl(2) = 2.3717(14), Ru(1)–Cl(1) = 2.3918(12), Cl(2)–Ru(1)–Cl(1) = 167.54(4), C(1)–Ru(1)–O(1) = 172.38(17), C(28)–Ru(1)–O(1) = 81.60(18), C(1)–Ru(1)–Cl(2) = 88.28(15), O(1)–Ru(1)–Cl(1) = 90.69(10).

second-generation complex. However, complex **10** additionally has a weak bonding interaction between the carbonyl oxygen of the amide group and the ruthenium center (Ru(1)–O(2) = 2.355 Å). This enhances their stability in air. The interatomic distances Ru(1)–O(1) for **10** between the ether oxygen and the metal Ru centers is only 2.171(3) Å and is shorter than **4** (2.257 Å) and **5a** (2.207 Å) containing ester groups. In addition, the interatomic distance (Ru(1)–O(2) = 2.355 Å) between the carbonyl group and the metal center is also shorter than **5a** (2.536 Å).

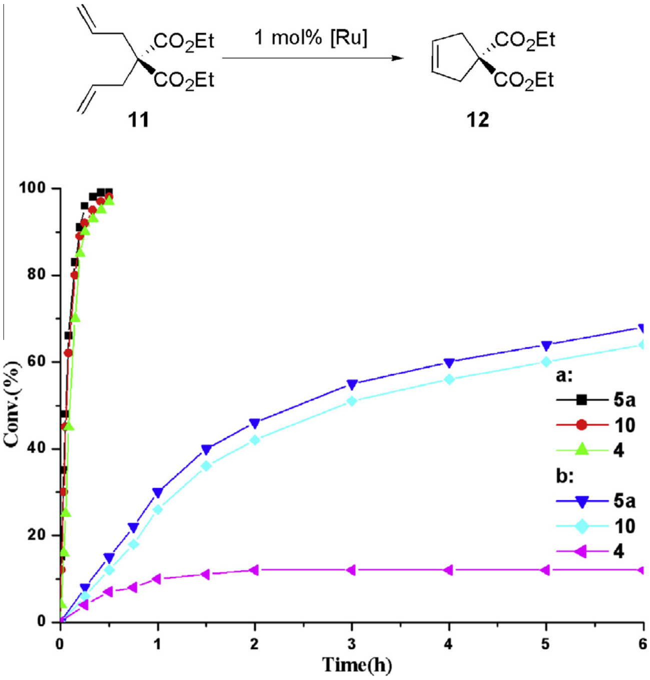


Fig. 2. Catalytic activities of **10**, **5a** and **4** in the RCM of diallyl diethylmalonate (CH_2Cl_2, 1 mol% ruthenium precatalyst): (a) 30 °C, 0.1 M, 30 min; (b) 0 °C, 0.02 M, 6 h, conversions calculated from ^1H NMR results.

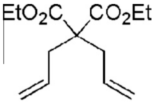
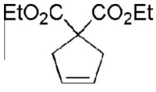
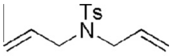
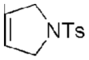
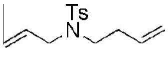
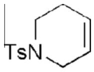
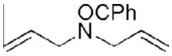
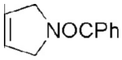
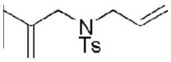
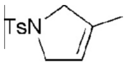
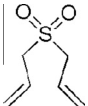
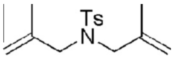
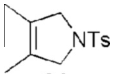
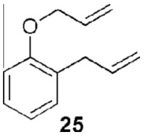
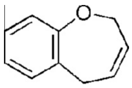
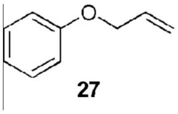
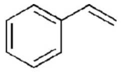
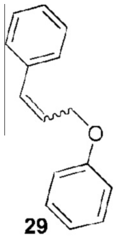
The catalytic activity of **10** for RCM was tested with diethyl diallylmalonate **11**. The relative conversion rates for RCM by **10** under similar conditions are shown in Fig. 2. At 30 °C, the catalytic activity of **10** is slightly higher than that of the unmodified **4**. All the catalysts, high RCM conversions of **11** (>97%) were achieved after 30 min at 30 °C. In order to clearly compare the efficiencies of two complexes, they were used in RCM reactions at 0 °C with the same substrate. The rate of initiation of the amide catalyst **10** was significantly higher than the unmodified **4**. The catalytic activity of **10** has an apparent enhancement. A good conversion is obtained after 6 h. This is similar to complex **5a**.

Further studies showed that catalyst **10** is also active for many other ring closures of substrates which containing nitrogen, oxygen and sulfur to result in the formation of either five-, six- or seven-membered rings with di- or tri-substituted double bonds (see Table 1). The products were obtained in high conversions at 35 °C with low catalyst loading (0.1 mol%). A specific example of the RCM is the bulky-substituted dienes **23**, a more challenging case. **10** gave good conversions at elevated temperatures (80 °C in toluene) with high catalyst loading (2.0 mol%) and a longer reaction time (24 h). Furthermore, in order to test the ability of our complex for the cross metathesis of olefins, **27** and **28** were selected and produced high yields of **29** when 2.5 mol% of catalyst was used (Table 1, entry 9).

3. Conclusions

A new double oxygen (the ether oxygen and the carbonyl oxygen) chelated ruthenium carbene metathesis catalysts was presented. The coordination of the carbonyl oxygen of the amide group and the ruthenium center gave additional protection to the metal center. This enhanced it stability in air and made it easier to purify with silica gel column chromatography. Interestingly, it exhibited higher activity and stability than the unmodified **4** in RCM and CM reactions for wide range substrates which containing nitrogen, oxygen and sulfur.

Table 1
Application of catalyst **10** to different substrates (0.5 M in CH_2Cl_2 or in toluene).

Entry	Diene	Product	Cat. (mol%)	Conditions[a]	Yield (%)[c]
1	 **11**	 **12**	0.1	0.5 h	98
2	 **13**	 **14**	0.1	0.5 h	99
3	 **15**	 **16**	0.1	0.5 h	99
4	 **17**	 **18**	0.1	0.3 h	99
5	 **19**	 **20**	0.1	1.0 h	98
6	 **21**	 **22**	0.1	0.5 h	98
7	 **23**	 **24**	2.5	24.0 h[b]	95
8	 **25**	 **26**	0.1	0.5 h	98
9	 **27**  **28**	 **29** Z:E>20;1	2.5	12.0 h	94

[a] Reactions were conducted at 35 °C in CH_2Cl_2.
[b] In toluene at 80 °C.
[c] Isolated yields after silica gel chromatography. Yields determined by ^1H NMR spectroscopy.

4. Experiment

4.1. Synthesis of ethyl-2-(4-methyl-2-(prop-1-enyl)phenoxy) propanoate *8*

A flask was charged with dry acetone (8 mL), K_2CO_3 (0.5 g, 3.7 mmol) and **7** (2.5 mmol). The mixture was heated to 50 °C and alpha bromo ethyl propionate (0.6 g, 3.3 mmol) was slowly added. Then, the reaction mixtures were stirred for 3 h under reflux. After cooling to room temperature, the mixtures were filtered and concentrated to afford the crude product. The crude product was purified by silica gel chromatography (pentanes: $CH_2Cl_2 = 1:1$). Colorless oil. Yield: 97.7%. *Anal.* Calc. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.51; H, 8.15%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.27 (t, $J = 6.3$ Hz, 3H), 1.64 (d, $J = 6.5$ Hz, 3H), 1.93 (q, $J = 6.6$ Hz, 3H), 2.29 (s, 3H), 4.22 (q, $J = 6.7$ Hz, 2H), 4.72 (q, $J = 6.3$ Hz, 1H), 5.99 (m, 1H), 6.62 (m, 2H), 6.93 (m, 1H), 7.24 (d, $J = 6.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ: 14.1, 18.6, 18.9, 34.4, 61.1, 73.1, 112.1, 115.3, 126.2, 127.1, 127.4, 128.0, 130.8, 137.2, 153.3, 172.4 ppm. IR (KBr) v: 3081, 2983, 2936, 2869, 1755, 1637, 1499, 1375, 1272, 1243, 1137, 1096, 1052, 870, 903, 805 cm^{-1}.

4.2. Synthesis of 2-(4-methyl-2-(prop-1-enyl)phenoxy)propanoic acid *9*

A flask was charged with **8** (2.1 mmol) and NaOH (6.2 mL, 10.0%). The reaction mixtures were stirred for 5 h under reflux. After cooling to 0 °C, HCl (6 M) was added until the pH was 3–4. Stirring was continued for 15 min at 0 °C. The precipitate was then filtered and washed with water. After drying the desired acids were obtained. Under N_2, the acid (1.2 mmol) was charged with $SOCl_2$ at 50 mL Schlenk. After the reaction, the mixture was stirred for 2 h under reflux, and then the $SOCl_2$ was removed. Next 2 mL of dry benzene and dimethylamine (40%, 2.0 eq) were added at 0 °C under N_2. The reaction mixture was stirred at room temperature for 12 h. The organic layer was removed and the aqueous layer was extracted with benzene. The organic layers were combined and washed with saturated salt water, dried over magnesium sulfate, filtered and concentrated. Purification by flash column chromatography on silica (CH_2Cl_2) gave the desired product. Light yellow oil. Yield: 67.7%. *Anal.* Calc. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.86; H, 8.48; N, 5.55%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.65 (d, J = 6.5 Hz, 3H), 1.94 (q, J = 6.6 Hz, 3H), 2.29 (s, 3H), 2.95 (s, 3H), 3.09 (s, 3H), 4.90 (q, J = 6.2 Hz, 1H), 6.01 (m, 1H), 6.65 (m, 2H), 6.95 (m, 1H), 7.28 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.6, 18.9, 34.4, 36.3, 36.5, 73.9, 112.0, 115.1, 126.1, 127.0, 127.2, 127.8, 130.6, 137.1, 153.1, 172.1 ppm. IR (KBr) v: 3061, 2934, 2933, 1661, 1455, 1444, 1366, 1234, 1110, 1061, 1044, 955, 733 cm^{-1}.

4.3. Preparation of complex **10**

To a Schlenk flask charged with Grubbs' catalyst **2** (0.42 g, 0.50 mmol) and CuCl (0.05 g, 0.50 mmol), compound **9** (0.6 mmol) in 10 mL dry dichloromethane was added at room temperature under N_2. The resulting mixture was stirred for 40 min at 40 °C. After being cooled to room temperature, the reaction mixture was filtered and the clear filtrate was collected. The solvent from the filtrate was evaporated under vacuum to give a residue. The residue was purified by silica gel chromatography (CH_2Cl_2: ethyl acetate = 2:1 or pentanes: ethyl acetate = 3:2 or1:1) to give the desired product as a green crystalline solid. Yield: 65.7%. *Anal.* Calc. for $C_{34}H_{43}Cl_2N_3O_2Ru$: C, 58.53; H, 6.21; N, 6.02. Found: C, 58.45; H, 6.21; N, 5.95%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.41 (d, J = 6.3 Hz, 3H), 2.38 (s, 3H), 2.40 (bs, 6H), 2.52 (bs, 12H), 2.77 (s, 3H), 2.79 (s, 3H), 4.10 (s, 4H), 5.23 (q, J = 6.6, 1H), 6.54 (d, J = 8.3 Hz, 1H), 6.75 (s, 4H), 7.08 (s, 4H), 7.28 (d, J = 8.4 Hz, 1H), 16.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.7, 21.4, 27.3, 36.2, 37.0, 51.9, 62.2, 73.4, 112.3, 129.4, 129.3, 129.6, 133.2, 138.3, 145.9, 149.4, 171.4, 210.5, 302.1 ppm. IR (KBr) v: 3033, 2912, 2845, 2735, 1946, 1628, 1475, 1445, 1415, 1233, 1217, 1129, 1103, 853, 571 cm^{-1}.

4.4. Kinetics study of **10**, **5a** and **4**

A Schlenk flask was charged with catalyst (0.02 mmol, 1.0 mol%) and CH_2Cl_2. The sample was equilibrated at 30 °C (or 0 °C) before diethyl diallylmalonate **11** was added via a syringe. Aliquots were taken from the reaction mixture at the appropriate times using a syringe and were quenched immediately with 0.1 mol/L PEI in CH_2Cl_2. The resulting solution was then subjected to short column chromatography to remove the Ru metal residue using CH_2Cl_2 as the eluent. The solvent from the collected solution was evaporated under vacuum. The conversion yield to substrates was determined by comparing the ratio of the integrals of the ^1H NMR methylene proton peaks in the starting material with those in the product. The results are shown in Fig. 2.

4.5. Catalytic study of the ruthenium carbenes **10**

The general procedure for metathesis reactions with ruthenium carbenes **10** was performed as follows: a certain amount of ruthenium carbene catalyst **10** (0.0005–0.0125 mmol) and a solution of the substrate (0.5 mmol) in 1.0 mL dry CH_2Cl_2 (or toluene) was mixed in a reaction flask under nitrogen. The reaction mixture was stirred for 0.3–24 h. At the end of the reaction (monitored by thin-layer chromatography (TLC)), the catalysts were separated by silica gel chromatography using CH_2Cl_2 as the eluent to remove trace amounts of Ru residues. Conversions were estimated by ^1H NMR spectroscopy and obtained by comparing the ratios of the integrals of the starting materials with those of products. The catalytic activities of ruthenium carbene **10** for a variety of substrates are shown in Table 1.

Acknowledgements

Financial supports from NSFC (21102102, 21072149, and 20872108) are gratefully acknowledged.

Appendix A. Supplementary data

CCDC 981748 contains the supplementary crystallographic data for complex **10**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] (a) P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, Angew. Chem., Int. Ed. 34 (1995) 2039;
(b) P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100;
(c) J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus, A.H. Hoveyda, J. Am. Chem. Soc. 121 (1999) 791;
(d) S. Gessler, S. Randl, S. Blechert, Tetrahedron Lett. 41 (2000) 9973;
(e) M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953;
(f) J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674;
(g) M. Scholl, T.M. Trnka, J.P. Morgan, R.H. Grubbs, Tetrahedron Lett. 40 (1999) 2247.

[2] (a) R.H. Grubbs, Ed. Handbook of Metathesis, vols. 1–3, Wiley–VCH, Weinheim, Germany, 2003.;
(b) R.R. Schrock, A.H. Hoveyda, Angew. Chem., Int. Ed. 42 (2003) 4592;
(c) T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18;
(d) A. Furstner, Angew. Chem., Int. Ed. 39 (2000) 3012;
(e) M. Schuster, S. Blechert, Angew. Chem., Int. Ed. 36 (1997) 2037;
(f) D. Astruc, New J. Chem. 29 (2005) 42.

[3] (a) F. Verpoort, J.C. Martins, Eur. J. Org. Chem. (2009) 655;
(b) B. De Clercq, F. Verpoort, Tetrahedron Lett. 43 (2002) 9101;
(c) J.J. Van Veldhuizen, S.B. Garber, J.S. Kingsbury, A.H. Hoveyda, J. Am. Chem. Soc. 124 (2002) 4954;
(d) J.J. Van Veldhuizen, D.G. Gillingham, S.B. Garber, O. Kataoka, A.H. Hoveyda, J. Am. Chem. Soc. 125 (2003) 12502;
(e) D.G. Gillingham, A.H. Hoveyda, Angew. Chem., Int. Ed. 46 (2007) 3860.

[4] (a) T.W. Funk, J.M. Berlin, R.H. Grubbs, J. Am. Chem. Soc. 128 (2006) 1840;
(b) J.M. Berlin, S.D. Goldberg, R.H. Grubbs, Angew. Chem., Int. Ed. 45 (2006) 7591;
(c) P.A. Fournier, S.K. Collins, Organometallics 26 (2007) 2945;
(d) T.W. Funk, Org. Lett. 11 (2009) 4998;
(e) B.K. Keitz, K. Endo, P.R. Patel, M.B. Herbert, R.H. Grubbs, J. Am. Chem. Soc. 134 (2012) 693;
(r) B.K. Keitz, A. Fedorov, R.H. Grubbs, J. Am. Chem. Soc. 134 (2012) 2040;
(g) B.K. Keitz, K. Endo, M.B. Herbert, R.H. Grubbs, J. Am. Chem. Soc. 133 (2011) 9686;
(h) K. Endo, R.H. Grubbs, J. Am. Chem. Soc. 133 (2011) 8525.

[5] (a) H. Wakamatsu, S. Blechert, Angew. Chem., Int. Ed. 41 (2002) 2403;
(b) A.M. Dunne, S. Mix, S. Blechert, Tetrahedron Lett. 44 (2003) 2733;
(c) H. Wakamatsu, S. Blechert, Angew. Chem., Int. Ed. 41 (2002) 794.

[6] (a) K. Grela, S. Harutyunyan, A. Michrowska, Angew. Chem., Int. Ed. 41 (2002) 4038;
(b) A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, J. Am. Chem. Soc. 126 (2004) 9318;
(c) S. Harutyunyan, A. Michrowska, K. Grela, Highly Active Ruthenium (Pre)catalyst for Metathesis, vol. 3, Wiley–Interscience, New York, 2004, p. 169;
(d) M. Bieniek, R. Bujok, M. Cabaj, N. Lugan, G. Lavigne, D. Arlt, K. Grela, J. Am. Chem. Soc. 128 (2006) 13652;
(e) M. Bieniek, C. Samojłowicz, V. Sashuk, R. Bujok, P. Śledź, N. Lugan, G. Lavigne, D. Arlt, K. Grela, Organometallics 30 (2011) 4144.

[7] (a) G.L. Wu, S.L. Cao, J. Chen, Z.L. Chen, Eur. J. Org. Chem. (2012) 6777;
(b) C.D. Varnado Jr., E.L. Rosen, M.S. Collins, V.M. Lynch, C.W. Bielawski, Dalton Trans. 42 (2013) 13251;
(c) K. Arumugam1, C.D. Varnado Jr., S. Sproules, V.M. Lynch, C.W. Bielawski, Chem. Eur. J. 19 (2013) 10866.;
(d) J.P. Moerdyk, C.W. Bielawski, Organometallics 30 (2011) 2278;
(e) E.L. Rosen, D.H. Sung, Z. Chen, V.M. Lynch, C.W. Bielawski, Organometallics 29 (2010) 250.