



## Efficient ruthenium metathesis catalysts containing carborane ligands

Guiyan Liu<sup>a,\*</sup>, Huizhu Zhang<sup>a</sup>, Xia Zhao<sup>a</sup>, Jianhui Wang<sup>b,\*\*</sup><sup>a</sup> College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Key Laboratory of Inorganic–Organic Hybrid Functional Material Chemistry, Ministry of Education, Tianjin Normal University, Tianjin 300387, PR China<sup>b</sup> Department of Chemistry, College of Science, Tianjin University, Tianjin 300072, PR China

## ARTICLE INFO

## Article history:

Received 11 May 2013

Received in revised form

23 August 2013

Accepted 5 September 2013

## Keywords:

Olefin metathesis

Ruthenium

Grubbs catalyst

Immobilization

Ionic liquid

## ABSTRACT

A first generation Hoveyda–Grubbs ruthenium complex with a closo-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> tag has been prepared. This new catalyst was tested in ring-closing metathesis (RCM) reactions and proved to be quite efficient. In addition, the recovery and reuse of a previously reported second generation Hoveyda–Grubbs ruthenium carbene complex bearing an ionic [nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> tag was further studied. When used in an ionic liquid, the catalyst can be conveniently recycled and reused with only a very slight loss of activity for the RCM of oxygen-containing and N-protected substrates with di- or trisubstituted double bonds.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

In the past decade, ruthenium catalysts **1**–**4** (Fig. 1) have been widely used in organic synthesis for olefin metathesis [1,2]. The robustness of **3** and **4** has made it desirable to make these catalysts more recyclable [3]. To do this, various strategies like immobilization have been employed [4,5]. Introducing an ion-appended ligand onto the ruthenium metal center is a very effective method of immobilizing transition metal catalysts [6]. However, most of the reported catalysts of this type have a cation-appended ligand on the ruthenium metal center. Previously, we reported catalysts **5** and **6** (Fig. 2) which have a carborane-tagged isopropoxy styrene ligand bound to a Ru carbene [7]. Ruthenium carbene complex **5** with a closo-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> tag has a high level of activity which is similar to that of **4** in the ring-closing metathesis (RCM) of a wide variety of di-, tri-, and even tetrasubstituted diene and enyne substrates. Complex **6** with an ionic [nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>−</sup> tag was found to exhibit an extremely high level of recyclability in the RCM reactions of *N,N*-diallyltosylamide. In this paper, a first generation Ru complex with a closo-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> tag is reported. In addition, an extension of our research on complex **6** was done.

## 2. Results and discussion

Scheme 1 illustrates the synthetic routes for the first generation Hoveyda–Grubbs ruthenium complex **8** with a closo-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> tag and complex **9** with an ionic [nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>−</sup> tag. The treatment of **7** with **1** in the presence of CuCl in CH<sub>2</sub>Cl<sub>2</sub> at 50 °C, as described by Hoveyda and co-workers [1 h], resulted in the complete exchange of the styrene group to give the air-stable brownish powder **8** in good yield (75.1%). This complex was fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as by elemental analysis. Reaction of compound **7** with tetrabutylammonium fluoride (TBAF) in a mixed solvent of THF and water opened the carborane cage to give an intermediate, followed by a ligand exchange with **1** to afford a brownish solid. This product is believed to be the anionic [nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>−</sup> tagged ruthenium complex **9**. However, complex **9** is unlike complex **6** which contains an *N*-heterocyclic carbene (a strong electron-donating ligand). The *N*-heterocyclic carbene enables the Ru metal center in **6** to bear more electron density than the Ru center in **9** which contains tricyclohexyl phosphine. The higher electron density in **6** prevents the Ru metal from coordinating with an electron-donating ligand or an anionic group. In contrast, the interaction between the anionic [nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>−</sup> group and the Ru metal center in **9** is strong enough to accelerate the decomposition of **9** and so complex **9** was unstable and could not be characterized and no catalytic activity for it could be detected.

\* Corresponding author. Fax: +86 022 2376653.

\*\* Corresponding author. Fax: +86 22 2740 3475.

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

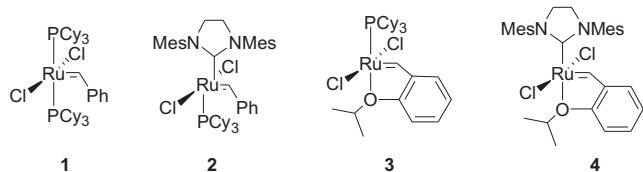


Fig. 1. Ru catalysts for olefin metathesis.

Complexes **5** and **8** were tested as catalysts for RCM reactions and the results are shown in Table 1. Like ruthenium carbene complex **5**, complex **8** is also an active RCM catalyst for the ring closures of the N-protected substrates **10**, **12**, and **14** and the oxygen-containing substrates **16** and **18**. These reactions resulted in the formation of five-, six-, or seven-membered rings with di-substituted double bonds. The products were obtained in high conversions with a low catalyst loading (0.2 mol %) (see Table 1). For the di-substituted diene **20** and the tri-substituted dienes (**22** and **24**), both complexes **5** and **8** gave low conversions with a low catalyst loading (0.2 mol %). However RCM was achieved in good conversions with a longer reaction time (12 h) when the catalyst loading was increased to 1.0 mol %. So, like complex **5**, **8** is an active catalyst for a large scope of RCM reactions, and it is tolerant to many functional groups. This behavior is similar to that of its parent compound **3**.

The recyclability and reusability of complex **6** for substrate **10** in an ionic liquid (IL, BMI·PF<sub>6</sub>) has previously been established [7]. In order to further investigate the reusability and recyclability of **6**, other di- and tri-substituted diene substrates were selected. The results are shown in Table 2. These reactions led to the formation of various carbocyclic olefins. Ruthenium carbene complex **6** which has an ionic [nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> tag can be recycled and reused 8 times for substrate **14** and 5 times for substrate **12** with 2.5 mol %. For the oxygen-containing diene **18**, catalyst **6** is also recyclable and high conversions were obtained. Even for the trisubstituted substrate **22**, catalyst **6** could be recycled and reused 6 times with 2.5 mol% loading. All the reactions proceeded smoothly and gave the corresponding cyclic olefin products in excellent yields. In contrast, a dramatic decrease in the conversion of substrates was found after the first run when **8** was used to promote RCM in ILs. Therefore, **6** is a recyclable catalyst that can be used in an IL for many different diene substrates.

Importantly, catalyst **6** is the first catalyst with an anion-appended ligand on the ruthenium metal center that has good recyclability and is easily recovered. In 2003, Guillemin and co-workers [3p,3q] and Yao [6e,6f] independently reported the synthesis of IL-supported catalysts with a cation-appended ligand for the ring-closing metathesis (RCM) of olefins. The recycling and recovery capability of complex **6** is similar to those catalysts.

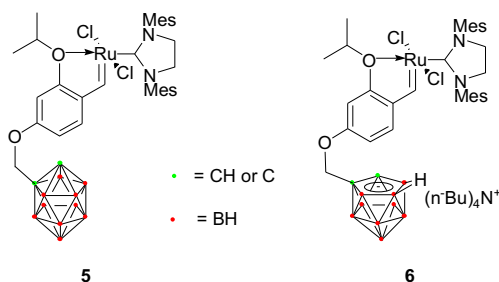


Fig. 2. Carbollide tagged ruthenium catalysts.

### 3. Conclusions

In conclusion, complex **8** with a closo-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> tag is an efficient catalyst for the RCM of di- and trisubstituted diene substrates. In addition it has been shown that ruthenium carbene complex **6** which has an ionic [nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> tag is a robust and recyclable RCM catalyst for the RCM of di- and trisubstituted diene substrates in an ionic solvent system. This catalyst has the combined advantages of high reactivity and a high level of recyclability and reusability. This work is useful for the continued development of catalyst systems that are suitable for organic transformations in ionic liquid.

### 4. Experiment

#### 4.1. General

<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>11</sup>B NMR spectra were acquired in CDCl<sub>3</sub> on Varian 400 spectrometers. If not otherwise noted, the chemical shift values are reported in ppm relative to residual CHCl<sub>3</sub> (δ 7.26) for the <sup>1</sup>H NMR spectra, relative to CDCl<sub>3</sub> (77.16 ppm) for the <sup>13</sup>C NMR spectra, and relative to BF<sub>3</sub>·OEt<sub>2</sub> (0.00 ppm) for the <sup>11</sup>B NMR spectra. Multiplicities are described using the following abbreviations: s = singlet, d = doublet, m = multiplet. Coupling constants (*J*) are quoted in Hz at 400 MHz for <sup>1</sup>H NMR.

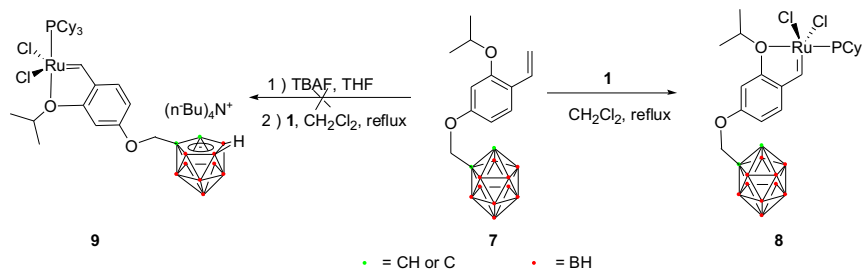
Infrared spectra were recorded on a Perkin–Elmer Model 1600 FT-IR spectrophotometer. Elemental analyses were determined at Nankai University using a Perkin–Elmer-2400C instrument. Conversions were obtained by HPLC analysis of the sample on an Agilent 1100 system using an Eclipse XDB-C8 (4.6 × 150 mm) column. The mobile phase was CH<sub>3</sub>OH/H<sub>2</sub>O = 4:1.

#### 4.2. Materials

Unless otherwise noted, all reactions were performed under an atmosphere of dry N<sub>2</sub> with oven-dried glassware and anhydrous solvents. THF, benzene, hexanes and diethyl ether were distilled with sodium/benzophenone under a N<sub>2</sub> atmosphere. CH<sub>2</sub>Cl<sub>2</sub> was dried over CaH<sub>2</sub> and distilled prior to use. All other solvents were dried over 4–8 Å mesh molecular sieves (Aldrich) and were either saturated with dry argon or degassed before use. Reactions were monitored by analytical thin layer chromatography (TLC) on 0.20 mm Anhui Liangchen silica gel plates and spots were detected by UV-absorption. Silica gel (200–300 mesh) (from Anhui Liangchen Chem. Company, Ltd.) was used for flash chromatography. The ionic liquid (BMI·PF<sub>6</sub>) was prepared and purified as reported previously and dried under high vacuum at 70 °C overnight to remove trace amounts of water. Compound **7** was prepared according to the literature method [7]. All other chemicals or reagents were obtained from commercial sources.

##### 4.2.1. Preparation of catalyst **8**

Grubbs catalyst I (411 mg, 0.50 mmol) was added to a flask with CuCl (50 mg, 0.50 mmol) under N<sub>2</sub>. A solution of 1-(3-isopropoxy-4-vinyl-phenoxy)-methyl-1,2-closo-1,2-carborane **7** (124 mg, 0.4 mmol) in dry dichloromethane (25 mL) was then poured into the reaction mixture. The resulting mixture was then stirred for 1 h at 50 °C. After cooling to room temperature, the reaction mixture was filtered to collect the filtrate. The solvent from the filtrate was evaporated under vacuum to give a residue. The residue was purified by flash column chromatography on silica using pentanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1) as the eluent to give the desired product **8** as a brownish powder (203 mg, 0.30 mmol, 75.1%). Analytical Data. Calcd (found) for: C<sub>31</sub>H<sub>57</sub>B<sub>10</sub>Cl<sub>2</sub>PO<sub>2</sub>Ru C, 48.18 (48.23); H, 7.43 (7.42). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 1.27 (m, 11H, CH<sub>3</sub> and

Scheme 1. Synthesis of ruthenium catalysts **8** and **9**.

PCy<sub>3</sub>), 1.70 (m, 23H, PCy<sub>3</sub>), 1.27 (br, 10H, BH), 2.17–2.34 (m, 5H, PCy<sub>3</sub>), 4.45 (s, 2H, CH<sub>2</sub>), 5.20 (m, 1H, CH), 6.50 (d, <sup>3</sup>J(H, H) = 7.6 Hz, H, CHar), 7.59 (d, <sup>3</sup>J(H, H) = 10.0 Hz, 1H, CHar), 17.22 (s, 1H, Ru=CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 22.0, 26.2, 27.6, 30.1, 35.6, 35.8, 57.8, 69.5, 71.0, 102.0, 106.8, 123.8, 140.5, 154.5, 158.2, 279.2. IR (KBr) ν: 2931, 2852, 2593 (Ru=C), 1596, 1445, 1387, 1324, 1261, 1165, 1125, 911, 846, 730, 679 cm<sup>−1</sup>.

#### 4.2.2. General procedure for RCM reactions

A weighed amount of ruthenium catalyst **5** or **8** and a solution of substrate in dry CH<sub>2</sub>Cl<sub>2</sub> were mixed in a reaction flask

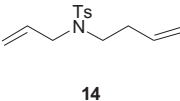
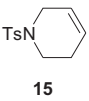
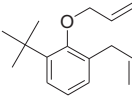
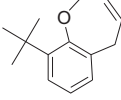
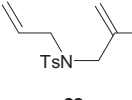
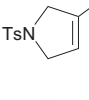
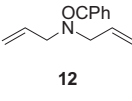
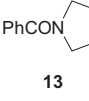
under nitrogen. The reaction mixture was stirred for 1.0–12 h at 40 °C. At the end of the reaction (monitored by thin-layer chromatography (TLC)), the catalysts were separated by silica gel chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluent to remove any trace amounts of Ru residue. Conversions were estimated by HPLC analysis. The starting materials and products were separated by silica gel chromatography. Yields were obtained by comparing the weight of the products of substrate with the weight of the starting substrate. The catalytic activities of complex **5** and **8** for a variety of substrates are shown in Table 1.

**Table 1**  
Application of catalysts **5** and **8** to different substrates.<sup>a</sup>

Entry	Substrate	Product	Cat. (mol %)	Conditions	Conv. (Yield)
1			<b>5</b> (0.2)	0.5 h	>98% (98%)
			<b>8</b> (0.2)	2.5 h	>98% (97%)
2			<b>5</b> (0.2)	0.3 h	>98% (97%)
			<b>8</b> (0.2)	2.0 h	>98% (97%)
3			<b>5</b> (0.2)	0.5 h	>98% (97%)
			<b>8</b> (0.2)	2.5 h	>98% (98%)
4			<b>5</b> (0.2)	0.5 h	>98% (96%)
			<b>8</b> (0.2)	3.5 h	>98% (96%)
5			<b>5</b> (0.2)	0.5 h	>98% (96%)
			<b>8</b> (0.2)	4.0 h	>98% (97%)
6			<b>5</b> (1.0)	8.0 h	>98% (96%)
			<b>8</b> (1.0)	12 h	>98% (96%)
7			<b>5</b> (1.0)	0.5 h	>98% (97%)
			<b>8</b> (1.0)	3.0 h	>98% (98%)
8			<b>5</b> (1.0)	8.0 h	>98% (96%)
			<b>8</b> (1.0)	12 h	>98% (95%)

<sup>a</sup> Reaction was conducted in CH<sub>2</sub>Cl<sub>2</sub> at 40 °C; conv. was obtained by HPLC; yields are isolated yields.

**Table 2**  
Recycling and reuse of **6** and **8** in BMI·PF<sub>6</sub>.

Substrate	Product	Catalyst	Cycle	Conv. <sup>a</sup> (%) (time)	Cycle	Conv. <sup>a</sup> (%) (time)
 14	 15	<b>6</b>	1	>98 (1.0 h)	5	>98 (1.0 h)
			2	>98 (1.0 h)	6	>98 (1.0 h)
			3	>98 (1.0 h)	7	>98 (1.0 h)
			4	>98 (1.0 h)	8	>98 (1.0 h)
		<b>8</b>	1	>98 (1.0 h)		>98 (5.0 h)
			2	<10 (12 h)		
 18	 19	<b>6</b>	1	>98 (5.0 h)	5	>98 (5.0 h)
			2	>98 (5.0 h)	6	>98 (5.0 h)
			3	>98 (5.0 h)	7	>98 (12 h)
			4	>98 (5.0 h)		
		<b>8</b>	1	>98 (8.0 h)		
			2	<10 (12 h)		
 22	 23	<b>6</b>	1	>98 (1.0 h)	4	>98 (1.0 h)
			2	>98 (1.0 h)	5	>98 (1.0 h)
			3	>98 (1.0 h)	6	>98 (12 h)
		<b>8</b>	1	>98 (2.0 h)		
			2	<10 (12 h)		
 12	 13	<b>6</b>	1	>98 (0.5 h)	4	>98 (0.5 h)
			2	>98 (0.5 h)	5	>98 (5.0 h)
			3	>98 (0.5 h)		
		<b>8</b>	1	>98 (1.0 h)		
			2	<10 (12 h)		

<sup>a</sup> Reactions were conducted at 35 °C using 2.5 mol % of catalyst in CH<sub>2</sub>Cl<sub>2</sub>; conv. obtained by HPLC; yields are isolated yields.

#### 4.2.3. Recycle study of ruthenium carbene **6** and **8** in an IL

The general procedure for RCM with **6** or **8** in an IL was performed as follows: catalyst **6** or **8** (2.5 mol % Ru), and 0.04 mL BMI·PF<sub>6</sub> in dry CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) were mixed in a reaction flask under N<sub>2</sub>. After the complete transfer of the catalyst from the organic phase to the ionic phase, a substrate (0.13 mmol) was introduced to the catalyst solution. The reaction mixture was stirred at 35 °C until the conversion of substrate was completed (monitored by TLC). Then the solvent was removed under vacuum and petroleum ether was added. The mixture was subjected to centrifugation to separate the ionic layer (containing the catalyst) and the product. The ionic layer (containing the catalyst) was then subjected to another cycle. The solvent from the organic solution was evaporated to afford the crude cyclized product. After purification by short column chromatography to remove any trace amounts of Ru residue, the sample was subjected to HPLC. Conversions were obtained by comparing the ratios of the peak areas of the starting materials with those of the products. The recycle data for the catalysts is shown in Table 2.

#### Acknowledgments

Financial supports from NSFC (21102102, 21072149, and 20872108) and the Doctoral Fund of Tianjin Normal University (52X09005 and 5RL110) are gratefully acknowledged.

#### References

- [1] (a) P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2039; (b) P. Schwab, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.* 118 (1996) 100; (c) J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, *J. Am. Chem. Soc.* 121 (1999) 2674; (d) J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus, A.H. Hoveyda, *J. Am. Chem. Soc.* 121 (1999) 791; (e) M. Scholl, T.M. Trnka, J.P. Morgan, R.H. Grubbs, *Tetrahedron Lett.* 40 (1999) 2247; (f) M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, *Org. Lett.* 1 (1999) 953; (g) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* 41 (2000) 9973; (h) S.B. Garber, J.S. Kingsbury, B.L. Gray, A.H. Hoveyda, *J. Am. Chem. Soc.* 122 (2000) 8168; (i) M.S. Sanford, J.A. Love, R.H. Grubbs, *Organometallics* 20 (2001) 5314; (j) K. Grela, S. Harutyunyan, A. Michrowska, *Angew. Chem. Int. Ed.* 41 (2002) 4038; (k) J.A. Love, J.P. Morgan, T.M. Trnka, R.H. Grubbs, *Angew. Chem. Int. Ed.* 41 (2002) 4035; (l) H. Wakamatsu, S. Blechert, *Angew. Chem. Int. Ed.* 41 (2002) 2403; (m) H. Wakamatsu, S. Blechert, *Angew. Chem. Int. Ed.* 41 (2002) 794; (n) M.B. Dinger, J.C. Mol, *Adv. Synth. Catal.* 344 (2002) 671; (o) A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, *J. Am. Chem. Soc.* 126 (2004) 9318; (p) M. Bieniek, R. Bujok, M. Cabaj, N. Lugan, G. Lavigne, D. Arlt, K. Grela, *J. Am. Chem. Soc.* 128 (2006) 13652.
- [2] (a) M. Schuster, S. Blechert, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2037; (b) R.H. Grubbs, S. Chang, *Tetrahedron* 54 (1998) 4413; (c) A. Frstner, *Angew. Chem. Int. Ed.* 39 (2000) 3012; (d) T.M. Trnka, R.H. Grubbs, *Acc. Chem. Res.* 34 (2001) 18; (e) R.R. Schrock, A.H. Hoveyda, *Angew. Chem. Int. Ed.* 42 (2003) 4592; (f) , in: R.H. Grubbs (Ed.), *Handbook of Metathesis*, vols. 1–3, Wiley-VCH, Weinheim, Germany, 2003.
- [3] (a) S.T. Nguyen, R.H. Grubbs, *J. Organomet. Chem.* 497 (1995) 195; (b) M. Ahmed, A.G.M. Barrett, D.C. Braddock, S.M. Cramp, P.A. Procopiou, *Tetrahedron Lett.* 40 (1999) 8657; (c) M. Ahmed, T. Arnauld, A.G.M. Barrett, D.C. Braddock, P.A. Procopiou, *Synlett* (2000) 1007; (d) S.C. Schürer, S. Gessler, N. Buschmann, S. Blechert, *Angew. Chem. Int. Ed.* 39 (2000) 3898; (e) L. Jafarpour, S.P. Nolan, *Org. Lett.* 2 (2000) 4075; (f) J. Dowden, J. Savovic, *Chem. Commun.* (2001) 37; (g) M. Mayr, B. Mayr, M.R. Buchmeiser, *Angew. Chem. Int. Ed.* 40 (2001) 3839; (h) J.S. Kingsbury, S.B. Garber, J.M. Giftos, B.L. Gray, M.M. Okamoto, R.A. Farrer, J.T. Fourkas, A.H. Hoveyda, *Angew. Chem. Int. Ed.* 40 (2001) 4251; (i) S. Randl, N. Buschmann, S.J. Connon, S. Blechert, *Synlett* 10 (2001) 1547; (j) L. Jafarpour, M.P. Heck, C. Baylon, H.L. Lee, C. Mioskowski, S.P. Nolan, *Organometallics* 21 (2002) 671; (k) S.J. Connon, A.M. Dune, S. Blechert, *Angew. Chem. Int. Ed.* 41 (2002) 3835; (l) K. Grela, M. Tryznowski, M. Bieniek, *Tetrahedron Lett.* 43 (2002) 9055; (m) S. Gibson, V.M. Swamy, *Adv. Synth. Catal.* 344 (2002) 619; (n) M. Mayr, M.R. Buchmeiser, K. Wurst, *Adv. Synth. Catal.* 344 (2002) 712; (o) S. Varray, R. Lazaro, J. Martinez, F. Lamaty, *Organometallics* 22 (2003) 2426;

- (p) N. Audic, H. Clavier, M. Mauduit, J.C. Guillemin, *J. Am. Chem. Soc.* 125 (2003) 9248;  
(q) H. Clavier, N. Audic, M. Mauduit, J.C. Guillemin, *Chem. Commun.* 20 (2004) 2282.
- [4] Reviews:  
(a) J.S. Kingsbury, A.H. Hoveyda, M.R. Buchmeiser, Wiley-VCH, Weinheim, 2003, p. 467. (b) M.R. Buchmeiser, *New J. Chem.* 28 (2004) 549;  
(c) H. Clavier, K. Grela, A. Kirschning, M. Mauduit, S.P. Nolan, *Angew. Chem. Int. Ed.* 46 (2007) 6786.
- [5] (a) G.Y. Liu, B. Wu, J.Z. Zhang, X.L. Wang, M.B. Shao, J.H. Wang, *Inorg. Chem.* 48 (2009) 2383;  
(b) G.Y. Liu, H.Y. He, J.H. Wang, *Adv. Synth. Catal.* 351 (2009) 1610;  
(c) G.Y. Liu, J.H. Wang, *Angew. Chem. Int. Ed.* 49 (2010) 4425.
- [6] (a) B. Mohr, D.M. Lynn, R.H. Grubbs, *Organometallics* 15 (1996) 4317;  
(b) D.M. Lynn, B. Mohr, R.H. Grubbs, *J. Am. Chem. Soc.* 120 (1998) 1627;  
(c) T.A. Kirkland, D.M. Lynn, R.H. Grubbs, *J. Org. Chem.* 63 (1998) 9904;  
(d) D.M. Lynn, B. Mohr, R.H. Grubbs, L.M. Henling, M.W. Day, *J. Am. Chem. Soc.* 122 (2000) 6601;  
(e) Q. Yao, Y. Zhang, *Angew. Chem. Int. Ed.* 42 (2003) 3395;  
(f) Q. Yao, M. Sheets, *J. Organomet. Chem.* 690 (2005) 3577;  
(g) H. Clavier, N. Audic, J.C. Guillemin, M. Mauduit, *J. Organomet. Chem.* 690 (2005) 3585;  
(h) A. Michrowska, K. Mennecke, U. Kunz, A. Kirschning, K. Grela, *J. Am. Chem. Soc.* 128 (2006) 13261;  
(i) W. Miao, T.H. Chan, *Acc. Chem. Res.* 39 (2006) 897.
- [7] G.Y. Liu, J.Z. Zhang, B. Wu, J.H. Wang, *Org. Lett.* 9 (2007) 4263.