

Note

Facile one-step synthesis of bis(NHC) ruthenium benzylidene catalyst for ring-closing metathesis

Wenzhen Zhang^a, Chenxi Bai^b, Xiaobing Lu^a, Ren He^{a,*}

^a State Key Laboratory of Fine Chemicals, Dalian University of Technology (DUT), 158 Zhongshan Rd., 116012 Dalian, China

^b Research Institute of Jilin Petrochemical Company Ltd., Petrochina, 132021 Jilin, China

Received 13 March 2007; received in revised form 11 April 2007; accepted 12 April 2007

Available online 21 April 2007

Abstract

Bis(NHC) ruthenium benzylidene complex $(\text{H}_2\text{IME})_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**9**) [H_2IME = 1,3-bis(2,6-dimethylphenyl)-4,5-dihydroimidazol-2-ylidene] was synthesized facilely by one-step reaction of $(\text{PPh}_3)_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**7**) with *N*-heterocyclic carbene (NHC) H_2IME (**6**). Complex **9** proved to exhibit remarkable catalytic activity for ring-closing metathesis (RCM) reaction at increased temperature.

© 2007 Elsevier B.V. All rights reserved.

Keywords: One-step synthesis; Bis(NHC) ruthenium complex; *N*-Heterocyclic carbene; RCM

1. Introduction

Ruthenium alkylidene complexes have been applied extensively as efficient metathesis catalysts in organic synthesis and polymer chemistry [1]. Bis(NHC) ruthenium alkylidene catalysts usually show relatively low catalytic activity at room temperature because the NHC ligand is difficult to dissociate from metal center to form catalytically active 14-electron intermediate by the accepted dissociative pathway [2]. However, those complexes exhibit extremely high catalytic efficiency at increased temperature presumably because the initiation is accelerated, and more importantly, their good thermal stability inhibits the significant decomposition of the catalysts [3].

The synthesis of bis(NHC) ruthenium alkylidene complexes can be achieved in several ways. Ruthenium alkylidene complexes contained two unsaturated NHC ligands can be easily prepared by reaction of $(\text{PPh}_3)_2(\text{Cl})_2\text{Ru}=\text{CHR}$ or $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru}=\text{CHR}$ with corresponding NHC ligands [4]. The reaction between $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**1**) [5] and asymmetrical saturated NHC with sterically small sub-

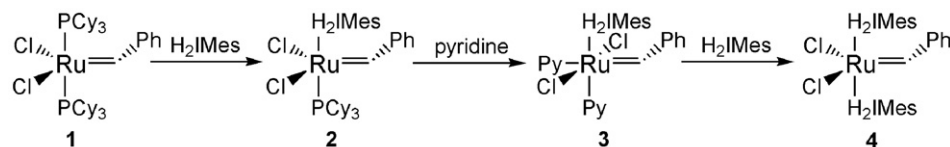
stituent can also afford corresponding bis(NHC) complex [6]. However, when complex **1** reacts with stereo-hindered saturated NHC ligand H_2IMes (H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene), monosubstituted complex $(\text{H}_2\text{IMes})(\text{PCy}_3)(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**2**) is formed exclusively [7], even with a large excess of H_2IMes . The phosphine exchange rate decreases dramatically when one of the PCy_3 ligands in complex **1** is replaced by one H_2IMes and thereby prevents further NHC ligand substitution to form bis(NHC) complex [2]. Consequently, bis(NHC) complex $(\text{H}_2\text{IMes})_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**4**) is prepared by reaction of $(\text{H}_2\text{IMes})(\text{C}_5\text{H}_5\text{N})_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**3**) [8] which contains more labile ligand with H_2IMes [3]. That means synthesis of bis(NHC) complex **4** from complex **1** requires three steps (Scheme 1). Herein, we describe facile one-step synthesis of ruthenium alkylidene complex **9** bearing two stereo-hindered saturated NHC ligands by circumventing the aforementioned synthesis method with three steps.

2. Results and discussion

In our beginning study, when complex **8** was prepared by reaction of $(\text{PPh}_3)_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**7**) [5] with 1.5 equiv. H_2IME (**6**) in unique hexane solvent (Scheme 2), small amounts (~10%) of bis(NHC) complex **5** was

* Corresponding author. Tel.: +86 411 88993861; fax: +86 411 83633080.

E-mail address: beyoudutmost@yahoo.com.cn (R. He).



Scheme 1.

formed and could be removed by repeated washes with methanol, which is evidently different from the aforementioned circumstance when complex **1** was used as reactant. This can be assigned to that the phosphine exchange rate of complex **8** is much (about 50 times) faster than that of complex **2** [9]. Accordingly further NHC coordination could be carried out in a dissociative ligand substitution pathway after one of the PPh₃ ligands in complex **7** had been replaced by one H₂IMe. Based on those knowledge, we assumed that bis(NHC) complex **9** could be achieved by one-step reaction of complex **7** with H₂IMe.

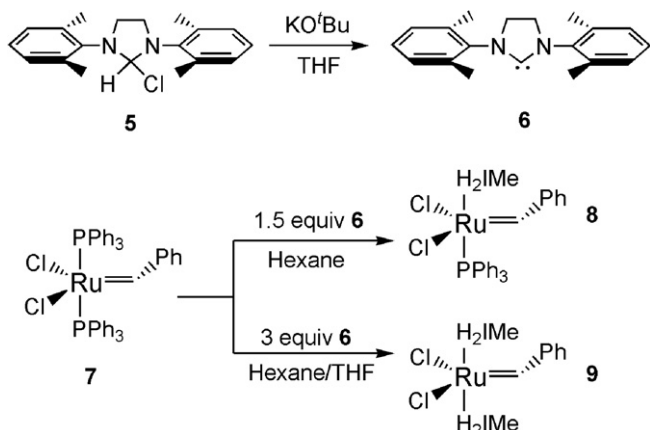
By reaction of complex **7** with 3 equiv. **6** in hexane/THF mixed solvent at 60 °C, complex **9** can be obtained successfully (Scheme 1). During the reaction, the initial green color of the suspension changed to dark red. After the solvent was filtered off and the remaining solid was washed several times with methanol and hexane, complex **9** was isolated as a dark red microcrystalline solid in 81% yield and with high purity. Noteworthy is that reaction in absolute THF or benzene solvent is performed more rapidly but gives relatively low yield of complex **9** probably because reactant complex **7** is prone to decompose. Complex **9** exhibits remarkable stability and can be stored in solution of CDCl₃ under ambient conditions without significant decomposition for several weeks.

Complex **9** was characterized by detailed spectroscopic studies. The diagnostic low-field benzyldiene proton resonance is found as singlet at 19.02 ppm in ¹H NMR spectroscopy. Compared to the corresponding resonance of this proton in complex **8** (19.25 ppm), a slight high field shift is observed. The benzyldiene carbon resonance

appears at 296.72 ppm in ¹³C NMR spectroscopy. HRMS analysis is in agreement with the calculated value.

To confirm the solid-state structure of the complex **9**, X-ray crystallography of complex **9** was studied. Suitable crystal for X-ray analysis was obtained by slow diffusion of pentane into saturated chloroform/hexane solution of the complex. The crystal structure plot is shown in Fig. 1. Crystal data and other details of the structure analysis are presented in Table 1. Important bond lengths and angles are summarized in Table 2. The coordination geometry of complex **9** is distorted square pyramid, where the two chloride ligands and the two NHC ligands are both in trans arrangement, the apical position is occupied by the benzyldiene ligand. The Ru–CNN bond lengths (Ru(1)–C(8): 2.103(3) Å, Ru(1)–C(27): 2.113(3) Å) of **9** are slightly longer than that of **8** (2.084(4) Å), maybe due to their bulky steric effect or mutually strong *trans* effect. Dihedral angles of the two NHC rings (24.1°) show that the two NHC ligands are somewhat staggered as a result of their steric demand. The angles of Cl(1)–Ru(1)–Cl(2) (164.44(3)°) and C(8)–Ru(1)–C(27) (165.04(10)°) in **9** are smaller than the angles of Cl(1)–Ru(1)–Cl(2) (165.45(5)°) and C(8)–Ru(1)–P(1) (167.54(13)°) in **8**.

The catalytic activity of complex **9** was tested in the RCM reaction of diethyl diallylmalonate and diallylmalononitrile (Scheme 3). As shown in Table 3, compared to good catalytic activity of complex **8** (entry 1), the bis(NHC) complex **9** exhibited rather low catalytic activity at low temperature (entry 3), which could be ascribed to its slow initiation. However, dramatically high catalytic efficiency was observed with complex **9** at increased temperature



Scheme 2.

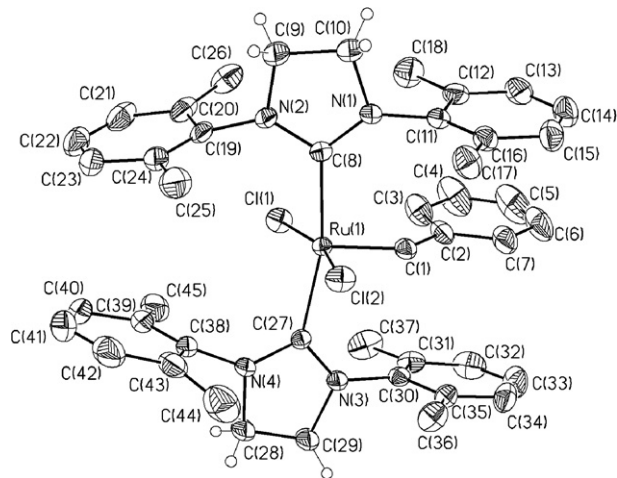
Fig. 1. Molecular structure of **9** with thermal ellipsoids drawn at 30% probability. Most hydrogen atoms have been omitted for clarity.

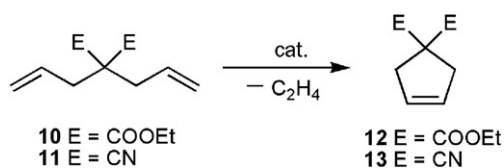
Table 1
Crystal data and structure refinement for complexes **8** and **9**

	Complex 8	Complex 9
Empirical formula	C ₄₄ H ₄₃ Cl ₂ N ₂ PRu	C ₄₆ H ₅₁ Cl ₅ N ₄ Ru (C ₄₅ H ₅₀ Cl ₂ N ₄ Ru · CHCl ₃)
Formula weight	802.74	938.23 (818.88, 119.35)
Crystallization solvent	Chloroform/Hexane/Pentane	Chloroform/Hexane/Pentane
Crystal habit	Block	Block
Crystal size (mm ³)	0.390.38 × 0.17	0.71 × 0.41 × 0.16
Crystal color	Red brown	Dark red
Wavelength Mo K α (Å)	0.71073	0.71073
Data collection temperature (K)	273(2)	273(2)
Unit cell dimensions	$a = 23.9341(2)$ Å, $\alpha = 90^\circ$ $b = 23.9341(2)$ Å, $\beta = 90^\circ$ $c = 44.5320(7)$ Å, $\gamma = 120^\circ$	$a = 15.6275(9)$ Å, $\alpha = 90^\circ$ $b = 11.8300(6)$ Å, $\beta = 103.465(3)^\circ$ $c = 24.9963(12)$ Å, $\gamma = 90^\circ$
Volume (Å ³)	22092.1(4)	4494.1(4)
Z	18	4
Crystal system	Rhombohedral	Monoclinic
Space group	<i>R</i> 3	<i>P</i> 2 ₁ / <i>n</i>
θ Range for data collection (°)	2.08–25.00	1.74–27.50
Completeness to θ_{\max}	99.7%	99.7%
Reflections collected	83120	28869
Independent reflections	8614 [$R_{\text{int}} = 0.0518$]	10304 [$R_{\text{int}} = 0.0318$]
Absorption coefficient (mm ⁻¹)	0.487	0.683
Data/restraints/parameters	8614/0/451	10304/0/505
Goodness-of-fit on F^2	0.962	1.032
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0578$, $wR_2 = 0.1904$	$R_1 = 0.0441$, $wR_2 = 0.1248$
<i>R</i> indices (all data)	$R_1 = 0.0775$, $wR_2 = 0.2103$	$R_1 = 0.0620$, $wR_2 = 0.1345$
Largest differences in peak and hole (e Å ⁻³)	1.329 and -0.393	0.924 and -0.672

Table 2
Selected bond lengths (Å) and angles (°) for complexes **8** and **9**

	Complex 8	Complex 9
<i>Bond lengths</i>		
Ru–C(1)	1.836(4)	1.831(3)
Ru–C(8)	2.084(4)	2.103(3)
Ru–Cl(1)	2.3819(13)	2.3636(8)
Ru–Cl(2)	2.3763(13)	2.3925(8)
Ru–P or Ru–C(27)	2.4045(11)	2.113(3)
<i>Bond angles</i>		
C(1)–Ru–C(8)	100.06(18)	96.36(12)
C(1)–Ru–Cl(1)	91.49(17)	103.52(11)
C(1)–Ru–Cl(2)	102.88(17)	91.95(11)
C(8)–Ru–Cl(1)	90.99(13)	94.05(8)
C(8)–Ru–Cl(2)	84.30(13)	85.71(8)
Cl(1)–Ru–Cl(2)	165.45(5)	164.44(3)
C(1)–Ru–P, or C(27)	92.22(14)	97.85(12)
C(8)–Ru–P, or C(27)	167.54(13)	165.04(10)

because of its good thermal stability (entry 4), while phosphine-contained complex **8** probably decomposed so fast that very low conversion was obtained (entry 2). Furthermore, when cyano-contained substrate diallylmalononitrile



Scheme 3.

Table 3
RCM reactions catalyzed by **8** and **9**.

Entry	E	Catalyst	Cat. mol %	Conv./% ^a
1 ^b	COOEt	8	2.0	91
2 ^c	COOEt	8	0.2	20
3 ^b	COOEt	9	2.0	28
4 ^c	COOEt	9	0.2	98
5 ^b	CN	8	5.0	44
6 ^c	CN	9	0.2	96

^a Conversion was determined by GC and confirmed by ¹H NMR.

^b 0.1 M substrate in CH₂Cl₂, 40 °C, 6 h.

^c 0.1 M substrate in PhCH₃, 80 °C, 6 h.

was used, complex **9** showed high resistance towards the cyano group and remained its high catalytic efficiency (entry 6) compared with low catalytic efficiency of complex **8** (entry 5).

3. Conclusion

We have described that ruthenium benzylidene complex **9** bearing two stereo-hindered saturated NHC ligands could be prepared by facile one-step reaction of complex **7** with corresponding *N*-heterocyclic carbene. The solid structure of complex **9** was confirmed by X-ray crystallography. Complex **9** proved to exhibit extremely high catalytic efficiency for RCM reaction at increased temperature and show high resistance towards the cyano group in RCM reaction of diallylmalononitrile.

4. Experimental

Manipulations of oxygen- and/or moisture-sensitive materials were performed using standard Schlenk techniques under a dry nitrogen atmosphere. Nuclear magnetic resonance spectra were recorded on a Varian Inova instrument (400 MHz for ^1H , 160 MHz for ^{31}P , 100 MHz for ^{13}C). High resolution mass spectra were recorded with a Q-TOF mass spectrometry (Micromass, England) equipped with Z-spray ionization source. Diethyl diallylmalonate [10] and diallylmalononitrile [11] were prepared according to literature procedures. Methylene chloride was dried over CaH_2 , distilled and stored under nitrogen. THF, toluene and hexane were dried and distilled from Na/benzophenone. All other reagents were of analytical grade quality purchased commercially and used as received unless noted otherwise.

4.1. Synthesis of complex 8

A 100-mL dried Schlenk flask was charged with 1,3-bis(2,6-dimethylphenyl)-4,5-dihydroimidazolium chloride (**5**) (1.08 g, 3.43 mmol, 1.5 equiv.) and dry THF (50 mL) under a nitrogen atmosphere. To this suspension was added potassium *tert*-butoxide (0.39 g, 3.48 mmol, 1.5 equiv.) at room temperature. The chloride salt dissolved immediately to give a cloudy yellow solution. The reaction mixture was allowed to stir at room temperature for 2 h, followed by removal of THF *in vacuo* and addition of dry hexane (60 mL), stirring for 10 min, and then filtration of this suspension to another 100-mL dried Schlenk flask which contained $\text{RuCl}_2(=\text{CHPh})(\text{PPh}_3)_2$ (**7**) (1.80 g, 2.29 mmol, 1.0 equiv.) under nitrogen. The reaction mixture was heated at 60 °C for 4 h, allowed to cool to room temperature and stirred for 6 h, at which time the original green color of reaction mixture changed to red. The red precipitate was then filtrated under nitrogen and was washed with anhydrous methanol (3 × 20 mL), hexane (3 × 20 mL) and dried *in vacuo* to give **8** as a red microcrystalline solid (1.57 g) in 85% yield. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 19.25$ (s, 1H, Ru=CHPh), 7.47–6.58 (multiple peaks, 26H, Ph_3P , *ortho* CH, *para* CH, *meta* CH, 2,6-dimethylphenyl aromatic CH), 4.12 (s, 2 H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.96 (s, 2H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.70 (s, 6H, *ortho* CH_3), 2.31 (s, 6H, *ortho* CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 292.28$ (m, Ru=CHPh), 219.70, 152.56, 139.67, 138.32, 137.41, 134.24, 132.23, 130.50, 129.38, 129.19, 128.68, 128.66, 128.43, 127.81, 127.64, 125.50, 51.90, 50.21, 21.63, 18.91. ^{31}P NMR (CDCl_3 , 160 MHz): $\delta = 37.3$ (s). HRMS (ESI), m/z : $[\text{M} - \text{Cl}]^+$, calculated: 767.1896, found: 767.1916.

4.2. Synthesis of complex 9

A 100-mL dried Schlenk flask was charged with 1,3-bis(2,6-dimethylphenyl)-4,5-dihydroimidazolium chloride (**5**) (2.10 g, 6.68 mmol, 3.0 equiv.) and dry THF (60 mL)

under a nitrogen atmosphere. To this suspension was added potassium *tert*-butoxide (0.75 g, 6.70 mmol, 3.0 equiv.) at room temperature. The chloride salt dissolved immediately to give a cloudy yellow solution. The reaction mixture was allowed to stir at room temperature for 2 h, followed by concentration of solvent *in vacuo* to ~5 mL and addition of dry hexane (60 mL), stirring for 10 min, and then filtration of this suspension to another 100-mL dried Schlenk flask which contained $\text{RuCl}_2(=\text{CHPh})(\text{PPh}_3)_2$ (**7**) (1.73 g, 2.20 mmol, 1.0 equiv.) under nitrogen. The reaction mixture was heated at 60 °C for 6 h, allowed to cool to room temperature and stirred for 2 h, at which time the original green color of reaction mixture changed to dark red. The red precipitate was then filtrated under nitrogen and was washed with anhydrous methanol (2 × 20 mL), hexane (3 × 20 mL) and dried *in vacuo* to give **9** as a dark red microcrystalline solid (1.46 g) in 81% yield. ^1H NMR (CDCl_3 , 400 MHz): $\delta = 19.02$ (s, 1H, Ru=CHPh), 8.87 (d, $J = 8.0$, 1H, CHPh), 7.10 (t, $J = 7.2$, 1H, CHPh), 6.96 (t, $J = 7.2$, 1H, CHPh), 6.90 (br. s, 8H, 2,6-dimethylphenyl aromatic CH), 6.63 (t, $J = 7.6$, 1H, CHPh), 6.52 (br. s, 2H, 2,6-dimethylphenyl aromatic CH), 6.00 (d, $J = 7.6$, 1H, CHPh), 5.83 (br. s, 2H, 2,6-dimethylphenyl aromatic CH), 3.60 (s, 8H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.28 (s, 24H, *ortho* CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 296.72$ (m, Ru=CHPh), 219.79, 150.85, 139.25, 137.73, 124.12, 132.19, 131.52, 130.31, 129.08, 128.28, 127.76, 126.93, 126.82, 52.16, 19.23. HRMS (ESI), m/z : $[\text{M} - \text{Cl}]^+$, calculated: 783.2767, found: 783.2755.

4.3. RCM procedure

In a typical experiment, catalyst **9** (3.6 mg, 4.4 μmol) and diallylmalononitrile (321 mg, 2.2 mmol) were weighed to a dried, two-necked flask equipped with a reflux condenser, 22 mL solvent was then added. The resulting mixture was stirred under the certain condition. After reaction was completed, the mixture was filtered through a short pad of silica gel, and the solvent was removed *in vacuo*. Conversion was measured by GC-FID and confirmed by NMR.

4.4. X-ray crystallography

Crystal data and other details of the structure analysis are presented in Table 1. Suitable crystal for X-ray diffraction was mounted on a glass fiber. Data collection was performed on a Bruker Smart APEX CCD diffractometer using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 273 K. The diffraction frames were integrated using the SAINT package. The structure was solved by direct methods using the program SHELXS97. Structure refinement by the full-matrix least-squares on F^2 was carried out with the program SHELXL97. All non-hydrogen atoms of the complex were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized

geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their respective parent atoms.

Acknowledgement

We thank Dr. Cheng He for X-ray crystallography analyses and helpful discussions.

Appendix A. Supplementary material

CCDC 635773 and 635776 contain the supplementary crystallographic data for **8** and **9**. These 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. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.04.014](https://doi.org/10.1016/j.jorganchem.2007.04.014).

References

- [1] (a) A. Fürstner, *Angew. Chem., Int. Ed.* 39 (2000) 3012–3043;
(b) R.H. Grubbs, *Tetrahedron* 60 (2004) 7117–7140;
(c) J.C. Mol, *J. Mol. Cat. A: Chem.* 213 (2004) 39–45;
(d) D. Astruc, *New J. Chem.* 29 (2005) 42–56;
- (e) E. Colacino, J. Martinez, F. Lamaty, *Coord. Chem. Rev.* 251 (2007) 726–764.
- [2] (a) M.S. Sanford, J.A. Love, R.H. Grubbs, *J. Am. Chem. Soc.* 123 (2001) 6543–6554;
(b) M.S. Sanford, M. Ulman, R.H. Grubbs, *J. Am. Chem. Soc.* 123 (2001) 749–750.
- [3] T.M. Trnka, J.P. Morgan, M.S. Sanford, T.E. Wilhelm, M. Scholl, T.L. Choi, S. Ding, M.W. Day, R.H. Grubbs, *J. Am. Chem. Soc.* 125 (2003) 2546–2558.
- [4] (a) T. Weskamp, W.C. Schattenmann, M. Spiegler, W.A. Herrmann, *Angew. Chem., Int. Ed.* 37 (1998) 2490–2493;
(b) J.C. Conrad, G.P.A. Yap, D.E. Fogg, *Organometallics* 22 (2003) 1986–1988;
(c) C. Marshall, M.F. Ward, T.A. Harrison, *J. Organomet. Chem.* 690 (2005) 3970–3975;
(d) J. Louie, R.H. Grubbs, *Angew. Chem., Int. Ed. Engl.* 40 (2001) 247–249.
- [5] P. Schwab, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.* 118 (1996) 100–110.
- [6] N. Ledoux, B. Allaert, A. Linden, P. Van Der Voort, F. Verpoort, *Organometallics* 26 (2007) 1052–1056.
- [7] M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, *Org. Lett.* 1 (1999) 953–956.
- [8] M.S. Sanford, J.A. Love, R.H. Grubbs, *Organometallics* 20 (2001) 5314–5318.
- [9] J.A. Love, M.S. Sanford, M.W. Day, R.H. Grubbs, *J. Am. Chem. Soc.* 125 (2003) 10103–10109.
- [10] N. Beaulieu, P. Deslongchamps, *Can. J. Chem.* 58 (1980) 875–877.
- [11] D. Enrique, A. de la Hoz, M. Andrés, S. Prado, *J. Chem. Soc., Perkin Trans.* (1991) 2589–2592.