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Synthesis, characterization and catalytic activity for ring-closing metathesis of ruthenium benzylidene complexes bearing *N*-heterocyclic carbene and bidentate phosphino-carboxylate ligands

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Abstract

New ruthenium benzylidene complexes (**3**) bearing *N*-heterocyclic carbene and chelating phosphino-carboxylate ligands were easily prepared by the reaction of $(H_2IMe)(PPh_3)(Cl)_2Ru{=}CHPh$ (**1**) [H_2IMe = 1,3-bis(2,6-dimethylphenyl)-4,5-dihydroimidazol-2-ylidene] with corresponding phosphino-carboxylates **2**. Catalysts featuring a five-membered or rigid six-membered chelating ring proved to exhibit enhanced stability and high catalytic efficiency toward the ring-closing metathesis (RCM) reaction of diethyl diallylmalonate and diallylmalononitrile.

Keywords: Metathesis; Ruthenium alkylidene; *N*-Heterocyclic carbene; Phosphino-carboxylate; RCM

1. Introduction

The continuous discovery of well-defined transition-metal alkylidene complexes as efficient homogeneous metathesis catalysts promoted olefin metathesis to a powerful tool in organic synthesis and polymer chemistry [1]. Ruthenium-based metathesis catalysts exhibited remarkable air and water stability, significant functional group tolerance [2] and thus have gained great attentions compared to molybdenum-based catalysts [3]. The second-generation Grubbs catalyst $(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh$ (**I**) introduced a saturated *N*-heterocyclic carbene (NHC) [4] to replace a single PCy_3 ligand of the first-generation Grubbs catalyst [5], which enhanced catalytic activity dramatically [6]. Continuative efforts to develop highly active catalysts led to the emergence of Hoveyda–Grubbs type [7], bispyridine [8] and bis(3-bromopyridine) [9] ruthenium alkylidene complexes. On the other hand, many studies focused on developing catalysts latent or applied at increased temperatures. In general, those special catalysts usually feature chelating alkylidene which is no longer involved in catalytic cycle after a catalytic turnover [10], or bear some exquisite chelating ligands at room temperatures, such as Shiff bases [11] and pyridinyl-alcoholates [12], and dissociate the donor ligand to open the chelating cycle and form catalytically active centers at elevated temperatures.

In this study, new ruthenium benzylidene metathesis catalysts containing *N*-heterocyclic carbene ligand and phosphino-carboxylate as the chelating ligand were prepared and characterized. The NHC ligand, which is well known to show excellent electron-donating property, should be difficult to dissociate from the metal center and accordingly stabilize catalytically active intermediate [13]. Phosphino-carboxylates, which have been used extensively as chelating ligands in homogeneous catalysis due to their easy accessibility and good flexibility [14,15], could dissociate the phosphine part to form catalytically active center at increased temperatures while the carboxylate part still linked to metal center.

2. Experimental

2.1. General procedures

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

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^{1}H, 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 a Z-spray ionization source. Benzene-d_6 was obtained from Aldrich and degassed prior to use. Phosphino-carboxylates [16], diethyl diallylmalonate [17] and diallylmalononitrile [18] 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.

2.2. Synthesis of (H_2IMe)(PPh_3)(Cl)$_2$Ru=CHPh (**1**) [19]

A 100-mL dried Schlenk flask equipped with a magnetic stirbar was charged with 1,3-bis(2,6-dimethylphenyl)-4,5-dihydroimidazolium chloride (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 $RuCl_2$(=CHPh)(PPh_3)$_2$ (1.80 g, 2.29 mmol, 1.0 equiv.) and equipped with a magnetic stirbar 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 **1** as a red microcrystalline solid (1.57 g) in 85% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 19.25 (s, 1H, Ru=C*H*Ph), 7.47–6.58 (multiple peaks, 26H, P*Ph*$_3$, *ortho*-C*H*, *para*-C*H*, *meta*-C*H*, 2,6-dimethylphenyl aromatic C*H*), 4.12 (s, 2H, NCH_2CH_2N), 3.96 (s, 2H, NCH_2CH_2N), 2.70(s, 6H, *ortho*-CH_3), 2.31 (s, 6H, *ortho*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 292.28 (m, Ru=*C*HPh), 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): δ = 37.3 (s). HRMS (ESI), *m/z*: [M–Cl]$^+$, calculated: 767.1896, found: 767.1916.

2.3. Synthesis of (H_2IMe)(κ^2(O,P)-PPh_2CH_2COO)(Cl)Ru=CHPh (**3a**)

A mixture of ruthenium complex **1** (570 mg, 0.71 mmol) and phosphino-carboxylate **2a** (305 mg, 1.15 mmol) in THF (60 mL) was stirred for 24 h at room temperature, over which time the color changed from red to brown. The reaction mixture was passed through a short pad of silica gel and the solution was concentrated *in vacuo* to a dark brown solid residue. The crude material was dissolved in a minimal volume ethyl acetate and loaded onto a plug of silica gel. Elution with ethyl acetate removed an orange band from the column. Concentration of the product fractions *in vacuo* removed the more solvent and precipitation of the catalyst with hexane, filtration and drying under vacuum afforded **3a** as a brown solid. Yield: 410 mg (0.55 mmol, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 18.86 (s, 1H, Ru=C*H*Ph), 7.45–6.48 (multiple peaks, 21H, *Ph*$_2$PCH$_2$COORu, *ortho*-C*H*, *para*-C*H*, *meta*-C*H*, 2,6-dimethylphenyl aromatic C*H*), 4.16 (bs, 4H, NCH_2CH_2N), 2.98 (dd, 2H, J = 16.4, 11.2, Ph$_2$PCH_2COORu), 2.67–2.36 (m, 12H, *ortho*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 301.33 (m, Ru=*C*HPh), 220.09 (d, Ru–*C*(N)$_2$, J_{CP} = 76), 180.64 (d, *C*OORu, J_{CP} = 14), 150.99, 139.41, 138.83, 136.90, 135.17, 132.24, 132.12, 131.99, 131.88, 130.76, 130.21, 129.82, 129.64, 128.99, 128.91, 128.64, 128.42, 128.20, 128.10, 51.73, 51.41, 32.92 (d, Ph$_2$P*C*H$_2$COORu, J_{CP} = 30), 18.83, 18.47. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 20.8 (s). HRMS (ESI), *m/z*: [M–Cl]$^+$, calculated: 713.1871, found: 713.1882.

2.4. Synthesis of (H_2IMe)(κ^2(O,P)-$PPh_2CH_2CH_2COO$)(Cl)Ru=CHPh (**3b**)

A mixture of ruthenium complex **1** (400 mg, 0.50 mmol) and phosphino-carboxylate **2b** (205 mg, 0.73 mmol) in THF (50 mL) was stirred for 40 min at room temperature, over which time the color changed from red to red brown. The reaction mixture was passed through a short pad of silica gel and the solution was concentrated *in vacuo* to a red brown solid residue. The crude material was dissolved in a minimal volume ethyl acetate and loaded onto a plug of silica gel. Elution with ethyl acetate and then THF removed an orange band from the column. Concentration of the product fractions *in vacuo* removed the more solvent and precipitation of the catalyst with hexane, filtration and drying under vacuum afforded **3b** as a pink orange solid. Yield: 310 mg (0.41 mmol, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 18.47 (s, 1H, Ru=C*H*Ph), 7.37–6.55 (multiple peaks, 21H, *Ph*$_2$PCH$_2$CH$_2$COORu, *ortho*-C*H*, *para*-C*H*, *meta*-C*H*, 2,6-dimethylphenyl aromatic C*H*), 4.28–4.08 (m, 4H, NCH_2CH_2N), 2.81–1.85 (m, 16H, Ph$_2$PCH_2CH_2COORu, *ortho*-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 305.71 (m, Ru=*C*HPh), 219.44 (d, Ru–*C*(N)$_2$, J_{CP} = 71), 177.58, 150.83, 140.48, 139.93, 139.15, 137.66, 137.16, 136.24, 134.26, 133.98, 132.84, 132.33, 131.08, 130.57, 129.87, 129.72, 129.19, 128.60, 128.19, 127.57, 51.40, 31.67, 21.57, 18.76, 18.55. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 26.1 (s). HRMS (ESI), *m/z*: [M–Cl]$^+$, calculated: 727.2027, found: 727.2043.

2.5. Synthesis of (H_2IMe)(κ^2(O,P)-o-$PPh_2C_6H_4COO$)(Cl)Ru=CHPh (**3c**)

A mixture of ruthenium complex **1** (300 mg, 0.37 mmol) and phosphino-carboxylate **2c** (180 mg, 0.55 mmol) in THF (50 mL) was stirred for 10 hours at room temperature, over which time the color changed from red to red brown. The reaction mixture was passed through a short pad of silica gel and the solution was concentrated *in vacuo* to a red brown solid residue. The crude material was dissolved in a minimal volume ethyl acetate and loaded onto a plug of silica gel. Elution with ethyl acetate removed an orange band from the column. Concentration of the product fractions *in vacuo*

removed the more solvent and precipitation of the catalyst with hexane, filtration and drying under vacuum afforded **3c** as a pink orange solid. Yield: 205 mg (0.25 mmol, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 18.62 (s, 1H, Ru=C*H*Ph), 7.42–6.35 (multiple peaks, 25H, $Ph_2PC_6H_4COORu$, *ortho*-C*H*, *para*-C*H*, *meta*-C*H*, 2,6-dimethylphenyl aromatic C*H*), 4.20–4.02 (m, 4H, NCH_2CH_2N), 2.69 (s, 3H, *ortho*-CH_3), 2.59 (s, 3H, *ortho*-CH_3), 2.30 (s, 3H, *ortho*-CH_3), 2.23 (s, 3H, *ortho*-CH_3). ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 33.4 (s). HRMS (ESI), *m/z*: $[M–Cl]^+$, calculated: 775.2027, found: 775.2003.

2.6. Procedure for RCM reaction of diethyl diallylmalonate [20]

The catalyst stock solution (0.020 M in C_6D_6, 25 μL, 0.50 μmol, 1.0 mol%) and C_6D_6 (0.47 mL) were added to an NMR tube sealed with a screw-cap. The sample was equilibrated at 40 °C in the NMR probe and then **4** (12 μL, 12.0 mg, 0.050 mmol, 0.1 M) was added via a syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **5** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.64 (d), with those in the product, δ 3.01 (s).

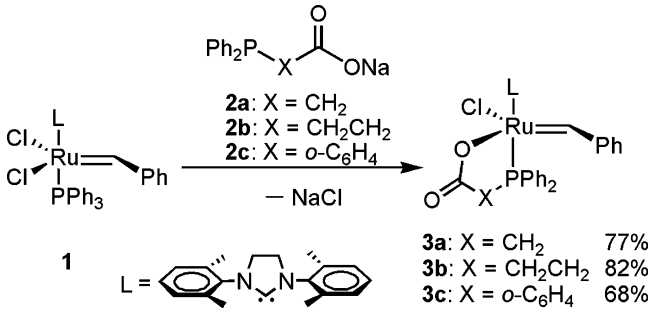
2.7. Procedure for RCM reaction of diallylmalononitrile

In a typical experiment, catalyst **3a** (3.2 mg, 4.3 μmol) and diallylmalononitrile (63 mg, 0.43 mmol) were weighed to a dried, two-necked flask equipped with a reflux condenser, and 4.3 mL solvent was then added. The resulting mixture was stirred under certain conditions. 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.

3. Results and discussion

3.1. Synthesis of the complexes

As shown in Scheme 1, the NHC phosphino-carboxylate complexes **3** were prepared by the reaction of complex **1** with corresponding sodium phosphino-carboxylates **2** in THF at room temperature according to a protocol used to obtain similar complexes [12]. One chloro ligand and one phosphine ligand of complex **1** were replaced with phosphino-carboxylate ligands under elimination of sodium chloride. It were anticipated that complexes **3a–c** would feature five-membered, flexible six-membered and rigid six-membered chelating rings respectively. Complexes **3a–c** were isolated in modest to good yields after facile column chromatography purification. Complexes **3** exhibit good oxygen and moisture tolerance and can be stored in air without significant decomposition after 4 weeks. Complexes **3** were characterized by detailed spectroscopic studies. In the ^{1}H NMR, the diagnostic low-field benzylidene proton resonance of **3** was found as singlet between 18.86 and 18.47 ppm. HRMS analyses were all in agreement with the calculated values.



Scheme 1. Preparation of the complexes.

3.2. X-ray crystallography

To confirm the solid-state structure of the complexes, crystals of **3a** and **3b** suitable for X-ray analyses were obtained by slow diffusion of pentane into saturated chloroform/hexane solution of the complexes. The structure plots are shown in Figs. 1 and 2. Important bond lengths and angles are summarized in Table 1. The coordination geometries of both complexes are distorted square pyramids, where the chloride ligands are trans to the carboxylate ligands, as are the phosphine ligands and NHC ligands and the apical positions are occupied by the benzylidene ligands. The Ru(1)–P(1) distances of **3a** (2.3347(10) Å) and **3b** (2.3609(8) Å) are shorter than that of **1** (2.4045(11) Å), maybe due to their less steric bulk and/or more electron donation from the phosphine parts. Effected by phosphino-carboxylate chelating ring, the angles of Cl(1)–Ru(1)–O(1) in **3a** and **3b** are widened to 170.05(9)° and 171.36(6)° compared with 165.45(5)° angle of Cl(1)–Ru(1)–Cl(2) in **1**. The larger P(1)–Ru(1)–C(1) (**3a**: 94.02(13)° versus **3b**: 90.16(9)°) and smaller P(1)–Ru(1)–C(8) (161.68(14)° versus 168.41(9)°), P(1)–Ru(1)–O(1) (81.39(8)° versus 90.60(6)°) bond angles illu-

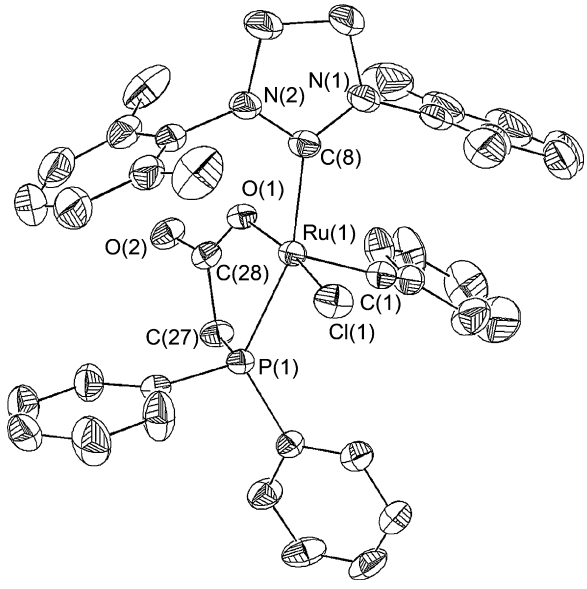


Fig. 1. Molecular structure of **3a** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

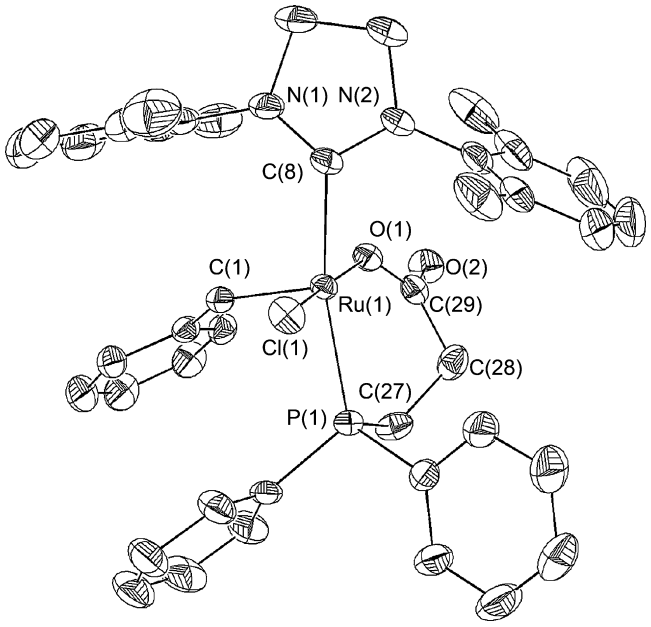


Fig. 2. Molecular structure of **3b** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

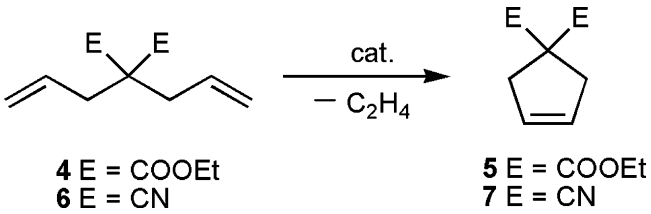
minate that **3a** embraces a more strained chelating ring and features a more crowded coordination environment.

*3.3. RCM reaction of diethyl diallylmalonate catalyzed by complexes **1**, **3** and **I***

The catalytic activity of complexes **3** was tested in the ring-closing metathesis of benchmark substrate diethyl diallylmalonate (**4**) employing the standard system (Scheme 2) [20]. As shown in Fig. 3 (reaction conditions: 1.0 mol %, 40 °C, C_6D_6), the NHC phosphino-carboxylate complexes **3** exhibited low catalytic activity at the relatively low temperature just like the analogous catalysts [11,12], which could be ascribed to their slow initiation resulting from additional stabilization of the chelating ligand. Interestingly, complex **3b** exhibited high initial activity and then decomposed quickly as PPh_3 containing complex **1** behaved [8(b)]. Instead, PCy_3 containing second-generation Grubbs catalyst **I** promote the reaction to completion within 0.5 h. Both complexes **3a** and **3c** were capable of catalyzing the reaction to completion at a given prolonged reaction time.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **3a**, **3b** and **1**

Bond lengths	Complex **3a**	Complex **3b**	Complex **1**
Ru–C(1)	1.828(5)	1.830(3)	1.836(4)
Ru–C(8)	2.080(4)	2.099(3)	2.084(4)
Ru–Cl(1)	2.3807(13)	2.3887(8)	2.3819(13)
Ru–O(1), Cl(2)	2.095(3)	2.097(2)	2.3763(13)
Ru–P	2.3347(10)	2.3609(8)	2.4045(11)
Bond angles	**Complex 3a**	**Complex 3b**	**Complex 1**
C(1)–Ru–C(8)	103.52(19)	101.42(12)	100.06(18)
C(1)–Ru–Cl(1)	89.45(16)	90.24(10)	91.49(17)
C(1)–Ru–O(1), Cl(2)	100.16(18)	98.00(11)	102.88(17)
C(8)–Ru–Cl(1)	90.02(13)	88.45(9)	90.99(13)
C(8)–Ru–O(1), Cl(2)	90.26(15)	87.36(10)	84.30(13)
Cl(1)–Ru–O(1), Cl(2)	170.05(9)	171.36(6)	165.45(5)
P–Ru–C(1)	94.02(13)	90.16(9)	92.22(14)
P–Ru–C(8)	161.68(14)	168.41(9)	167.54(13)
P–Ru–O(1), Cl(2)	81.39(8)	90.60(6)	90.93(5)



Scheme 2. Ring-closing metathesis reaction.

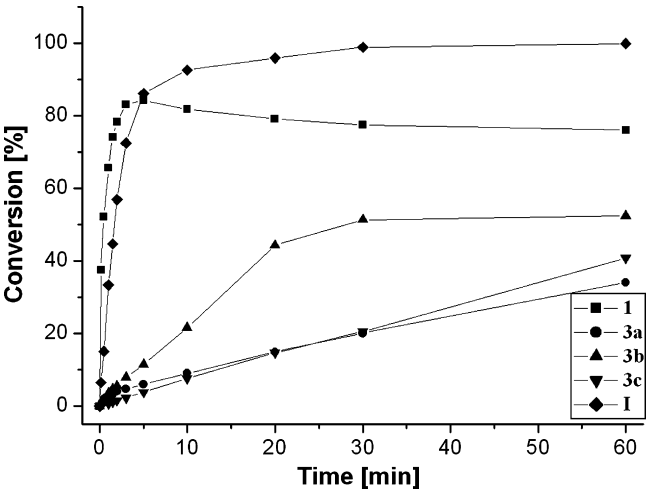


Fig. 3. Conversion plot for RCM of **4** using **1**, **3a–c** and **I** (1.0 mol %, 40 °C, C_6D_6).

Complexes **3** showed higher catalytic activity at elevated temperature rationally (Fig. 4, reaction conditions: 0.5 mol %, 70 °C, C_6D_6). Catalysts **1** and **3b** decomposed so fast at elevated temperature that they could not promote the reaction to completion.

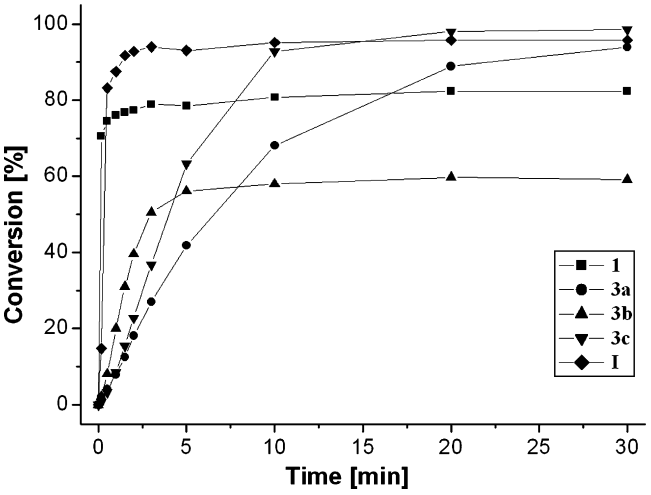


Fig. 4. Conversion plot for RCM of **4** using **1**, **3a–c** and **I** (0.5 mol %, 70 °C, C_6D_6).

However, **3a** and **3c** exhibited rather high stability and reactivity, presumably because their phosphine parts were relatively prone to protect or stabilize the catalytically active intermediate. The second-generation Grubbs catalyst **I** also showed highly catalytic activity but significant decomposition of catalyst was observed at elevated temperature [21].

In a separated experiment (reaction condition: 0.2 mol %, 80 °C, 6 h, 0.1 M **4** in $PhCH_3$), complexes **3a** and **3c** gave 92% and 87% conversion respectively, compared to modest conversion (67%) for the second-generation Grubbs catalyst I and poor performance of complexes **3b** (conversions <42%) and **1** (conversions <25%), which also suggested that complexes **3a** and **3c** exhibited enhanced stability and thus showed higher catalytic efficiency at increased temperature.

*3.4. RCM reaction of diallylmalononitrile catalyzed by complexes **1**, **3** and **I***

Cyano-containing substrate diallylmalononitrile (**6**) was also chosen to evaluate the catalytic activity of complexes **3** (Scheme 2). It is well known that cyano-containing substrates remained challenging for most metathesis catalysts because of their proneness to deactivate or destroy catalysts [22]. We anticipated that catalysts **3a** and **3c** could show resistance towards the cyano group because of their good stability. As shown in Table 2, low conversion was obtained for catalyst **1** at low temperature even with a high catalyst loading (entry 1). Reaction at high temperature gave modest conversion, and additionally, significant amount of isomerized substrate and product (∼20%) were observed which implied decomposition of the catalyst (entry 6) [21]. The second-generation Grubbs catalyst **I** showed good catalytic activity compared to catalyst **1** but ∼8% amount of isomerized substrate and product were also observed at increased temperature (entry 7). Catalysts **3a** and **3c** exhibited good resistance towards the cyano group and gave high conversion regardless of temperature change. More importantly, very small amount of isomerized substrate and product (∼2%) were observed at high temperature (entries 3, 5, 8, 10). That is presumably because their phosphine parts in the chelating ligands of **3a** and **3c** could protect the catalytically active intermediate from being deactivated or destroyed by the cyano group.

Table 2
RCM reactions of diallylmalononittrile[a]

Entry	Catalyst	Catalyst (mol %)	Conversion (%)[a]
1[b]	**1**	5.0	44
2[b]	**I**	5.0	96
3[b]	**3a**	2.0	90
4[b]	**3b**	2.0	69
5[b]	**3c**	2.0	95
6[c]	**1**	5.0	78
7[c]	**I**	5.0	91
8[c]	**3a**	1.0	98
9[c]	**3b**	1.0	63
10[c]	**3c**	1.0	83

[a] Conversion was determined by GC and confirmed by ^{1}H NMR.
[b] 0.1 M substrate in CH_2Cl_2, 40 °C, 12 h
[c] 0.1 M substrate in $PhCH_3$, 80 °C, 6 h.

4. Conclusion

New ruthenium metathesis catalysts **3** bearing NHC and chelating phosphino-carboxylate ligands could be easily synthesized by the reaction of $(H_2IMe)(PPh_3)(Cl)_2Ru{=}CHPh$ with corresponding phosphino-carboxylates. Compared to the catalysts bearing a six-membered chelating ring (**3b**) and $(H_2IMe)(PPh_3)(Cl)_2Ru{=}CHPh$ (**1**), catalysts featuring a five-membered (**3a**) or rigid six-membered (**3c**) chelating ring proved to exhibit obviously enhanced stability and high catalytic efficiency toward the RCM reaction of diethyl diallylmalonate and diallylmalononitrile, especially at increased temperature.

5. Supplementary material

CCDC 635773, 635774 and 635775 contain the supplementary crystallographic data for complexes **1**, **3a** and **3b**. 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 email: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.05.043.

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