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Synthesis and reactivity of oxygen chelated ruthenium carbene metathesis catalysts

Yiran Zhang [a], Mingbo Shao [b], Huizhu Zhang [a], Yuqing Li [a], Dongyu Liu [a], Yu Cheng [a], Guiyan Liu [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

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ABSTRACT

The rate of initiation of Hoveyda catalysts is affected by the electronic and steric effects that act upon the Ru···O coordination. In order to boost the activity of Hoveyda catalysts, a series of new oxygen chelated ruthenium carbene metathesis catalysts containing an *N*-heterocyclic carbene (NHC) and a carbonyl group has been developed, and their catalytic activities for olefin metathesis reactions were investigated. The aliphatic end groups of complexes $(H_2IMes)(Cl)_2Ru{=}C(H)[(C_6H_3X)OCH(Me)(C(O)OEt)(X = H, OMe, Me, NO_2)]$ were functionalized by the attachment of a straight-chain ester. The X-ray structures of complex $(H_2IMes)(Cl)_2Ru{=}C(H)[(C_6H_4)OCH(Me)(C(O)NMe_2)]$ 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. However, the carbonyl oxygen of complexes $(H_2IMes)(Cl)_2Ru{=}C(H)[(C_6H_3X)OCH(CH_2C(O)OCH_2)(X = H, OMe)]$ does not coordinate to the metal due to the steric effect of the lactone. All these complexes were used as catalysts for olefin metathesis reactions and all exhibited excellent performances for the ring-closing metathesis (RCM) of diethyl diallymalonate at 30 °C. The initiation rate of these catalysts was higher than that for the Hoveyda catalyst $((H_2IMes)(Cl)_2Ru{=}C(H)(C_6H_4\text{-}2\text{-}O^iPr))$ and these complexes are also active for cross metathesis (CM).

1. Introduction

Since the discovery of well-defined modern ruthenium catalysts **1**–**4** (Chart 1) [1], olefin metathesis as one of the most important tools for constructing carbon–carbon double bonds has been widely used in organic synthesis, materials science, and biochemistry [2]. Among these complexes, Grubbs second-generation ruthenium carbene catalyst **2** possesses a high activity and an excellent tolerance for a variety of functional groups. Ruthenium-benzylidene catalyst **4** which bears *N*-heterocyclic carbene (NHC) ligand, exhibits extraordinary activity and stability was introduced by Hoveyda and coworker [1c]. It is widely used in reuse and immobilization of the catalyst [3–5]. However, a large isopropoxy group and the donation of an electron from ^{i}PrO to ruthenium cause this catalyst to initiate more slowly than Grubbs catalyst **2**.

In 2002, Wakamatsu and Blechert synthesized complex **5** by modifying the neighboring bulky phenyl group [6]. This phenyl ruthenium catalyst lead to greatly increased initiation rates for different metathesis reactions even at 0 °C. Around the same time, Grela et al. developed complex **6** which has an electron-withdrawing substituent (a nitro group) [7]. Under very mild conditions (even at 0 °C) it was successfully applied to various types of olefin metathesis (ring-closing metathesis, cross metathesis and enyne metathesis). Both complexes **5** and **6** destabilize the oxygen/metal interaction which favors faster access to the formation of the 14-electron Ru carbene species; these results in increasing catalytic activity [8].

However, as mentioned by Conrad et al. [9], the global efficiency of an olefin metathesis catalyst not only has a high initiation rate and a high selectivity, but also has extraordinary stability and the stability of the precatalyst plays an important role. In order to boost the stability of the catalyst, many improvements have been made including changing the *N*-heterocyclic carbine [10] and the leaving group [11]. So, many highly efficient and stable Ru carbene metathesis catalysts have been designed based on complex **4** [12,13].

Complex **7a** and **7b** were developed by Bieniek et al., in 2006 [12b]. The aliphatic end groups of the complexes were functionalized by attaching an ester group which enhanced the leaving group

* Corresponding author. Fax: +86 022 23766532.
** Corresponding author. Fax: +86 22 27403475.
E-mail addresses: guiyanliu2013@163.com (G. Liu), wjh@tju.edu.cn (J. Wang).

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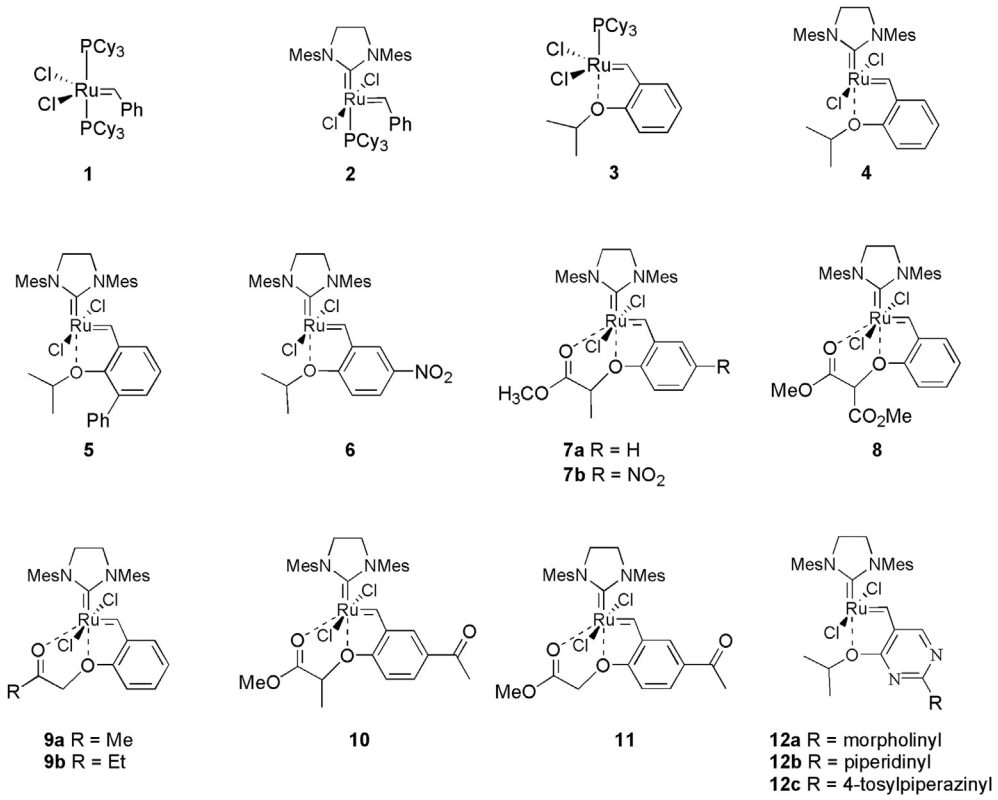


Chart 1. Ruthenium metathesis catalysts.

properties of the styrenyl ether. X-ray results showed that the carbonyl oxygen of the ester group in these complexes coordinated to the metal. Furthermore, complex **7b** which has an electron withdrawing NO_2 group gave high turnover numbers.

The rate of initiation of chelated complexes is affected by the electronic and steric effects that act upon the Ru···O coordination. In 2011, Bieniek et al. synthesized a series of complexes **8**–**11** with different substituents (an ester group, a ketonic group, or a malonic

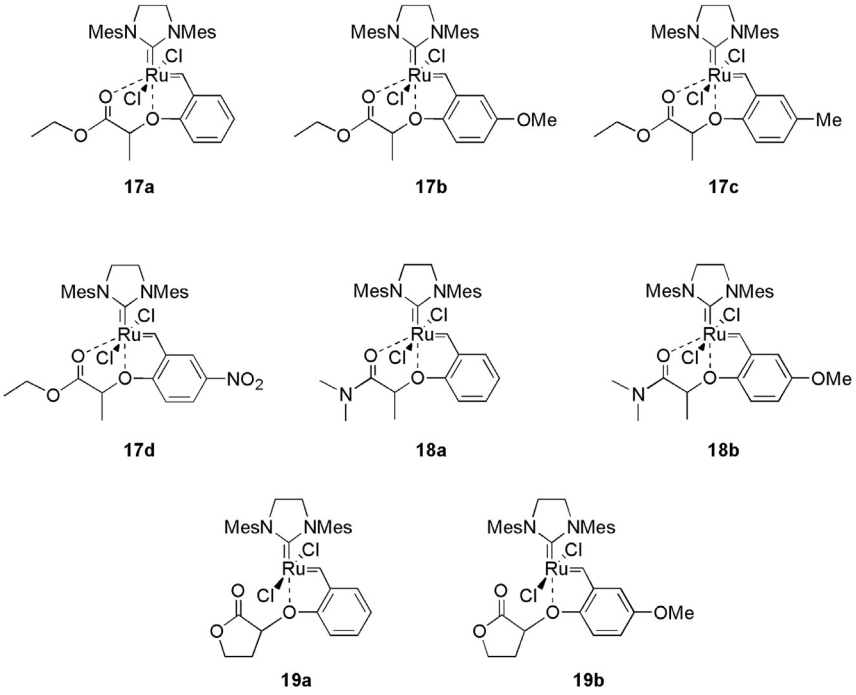
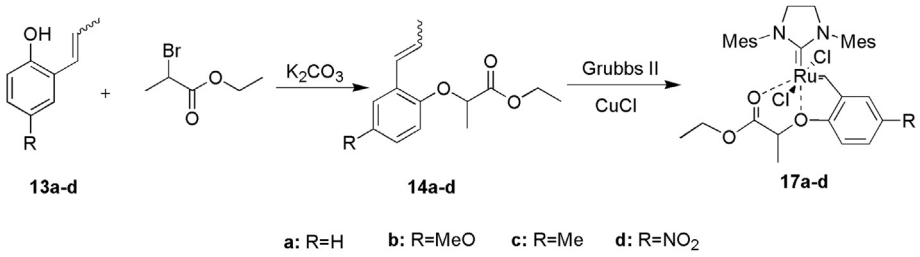
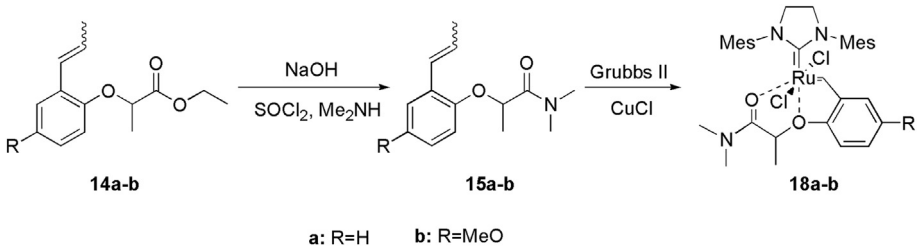


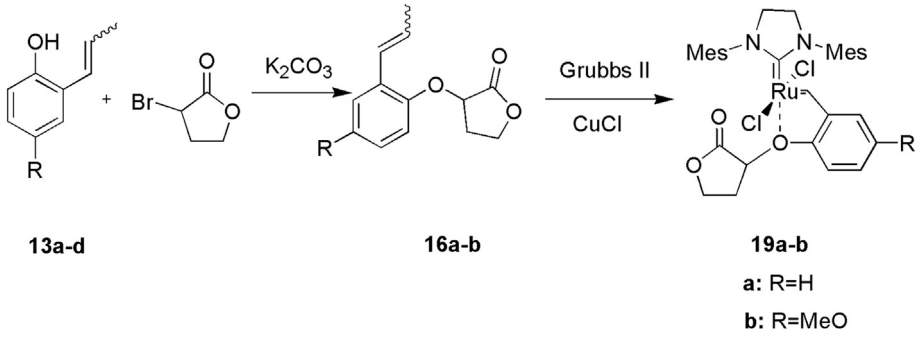
Chart 2. New oxygen chelated ruthenium carbene metathesis catalysts.



Scheme 1. Synthesis of ruthenium carbonyl **17** complexes.



Scheme 2. Synthesis of ruthenium carbonyl **18a** and **18b** complexes.



Scheme 3. Synthesis of ruthenium carbonyl **19a** and **19b** complexes.

group). All of these complexes had an additional functional group the coordinated to the metal center [12c]. 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. Recently, Wu et al. replaced the phenyl group with an electron-deficient pyrimidine unit and prepared a new type of *N*-heterocyclic carbene catalyst **12** [13]. The presence of an electron-deficient pyrimidine structure greatly enhanced the catalytic activities of the new NHC ruthenium complex. In addition, other methods have been used, including the changes of NHC-systems [14].

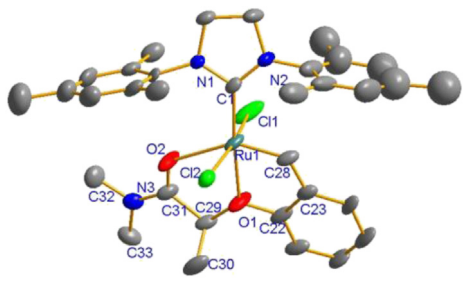


Fig. 1. Perspective view of the catalyst **18a**. Ellipsoids are drawn at the 50% probability level.

On the basis of these previous research; a series of new NHC ruthenium complexes **17**, **18** and **19** (Chart 2) in which the leaving group properties of the styrenyl ether were enhanced by attaching an ester or amide functional group to the aliphatic end group is reported herein.

2. Results and discussion

The synthesis of some new ethoxycarbonyl substituted complexes is depicted in Scheme 1. Ester-substituted styrenyl ethers were prepared as carbene ligand precursors by reacting commercially available **13a**–**d** with 2-bromo-propionic acid ethyl ester in the presence of potassium carbonate. The precursors (**14a**–**d**) were then reacted with a Grubbs second-generation catalyst in the presence of copper (I) chloride in CH_2Cl_2 at 40 °C, as described by Kingsbury et al. [1c]. This resulted in the exchange of the styrene

Table 1
Selected bond angles (deg).

	Cl(1)–Ru(1)–Cl(2)	C(1)–Ru(1)–O(1)	C(28)–Ru(1)–O(1)	C(1)–Ru(1)–Cl(2)	O(1)–Ru(1)–Cl(1)
18a	168.159(106)	172.234(332)	80.581(383)	96.104(304)	82.867(199)
19a	159.590(35)	177.635(118)	78.916(144)	92.988(99)	85.693(68)
19b	154.391(104)	178.518(336)	80.509(335)	97.293(297)	84.675(205)

Table 2
Selected interatomic distances (Å).

	Ru(1)–C(28)	Ru(1)–C(1)	Ru(1)–Cl(1)	Ru(1)–Cl(2)	Ru(1)–O(1)	Ru(1)–O(2)
18a	1.820	1.978	2.363	2.385	2.186	2.348
19a	1.828	1.974	2.364	2.345	2.242	
19b	1.806	2.037	2.315	2.265	2.341	

group to give the desired catalysts in good yield (**17a**-62.6%, **17b**-64.2%, **17c**-62.6%, and **17d**-67.7%) as greenish crystalline solids.

The synthesis of amide substituted complexes **18a** and **18b** is shown in Scheme 2. The *N*,*N*-dimethyl substituted carbene ligand amide precursors (**15a**,**b**) were obtained by hydrolysis and acylation of **14a**,**b**. An exchange reaction between **15a**,**b** and a Grubbs second-generation catalyst in the presence of copper(I) chloride afforded the desired catalysts **18a** and **18b**, in good yields (66.8%, to 65.2% respectively) in the form of green crystalline compounds.

Scheme 3 illustrates the synthesis of new ring lactone substituted Grubbs/Hoveyda second-generation catalysts. Ring lactone substituted styrenyl ethers **16a** and **16b** were prepared as carbene ligand precursors by the reaction of commercially available **13a** and **13b** with 3-bromo-dihydrofuran-2-one in the presence of potassium carbonate. These precursors were then reacted with a Grubbs second-generation catalyst in the presence of copper(I) chloride in CH_2Cl_2 at 40 °C, to give the desired catalysts **19a** and **19b** in good yields (64.0% and 64.2%) as greenish crystalline solids.

Crystals of the new Ru complex **18a** was grown by slow evaporation from CH_2Cl_2/ethyl acetate. The molecular structures of the two complexes are shown in Fig. 1. Some of the interatomic distances and bond angles are given in Tables 1 and 2. The X-ray structures show that the arrangements of the ligands around the metal centers have characteristics in common with those found in the Grubbs/Hoveyda second-generation complex. However, **18a** additionally has a weak bonding interaction between the carbonyl oxygen of the ester group and the ruthenium center. This enhances their stability in air and makes them easier to purify with silica gel column chromatography. The interatomic distances (Ru(1)–O(2) = 2.348 Å for **18a**) between the carbonyl groups and the metal Ru centers are shorter than those for complexes (**7**–**11**) containing ester groups.

Complexes **19a** and **19b** are different from **18a** in that the carbonyl oxygen does not coordinated with the metal center due to the effect of the five membered lactone ring. In **19a** and **19b**, only the ether oxygen coordinated with the Ru. The X-ray structures are shown in Fig. 2.

The catalytic activity of **17**, **18** and **19** for RCM was tested with diethyl diallylmalonate **20** and diallyltosylamide **22**. The relative

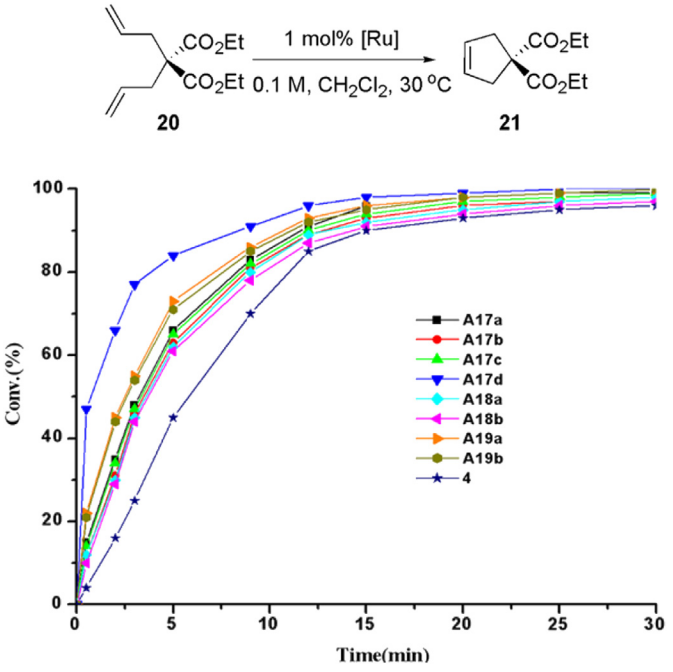


Fig. 3. Catalytic activities of **17**, **18**, **19** and **4** in the RCM of diallyl diethylmalonate (CH_2Cl_2, 1 mol % ruthenium precatalyst), 30 °C, 30 min, conversions calculated from ^1H NMR results.

conversion rates for RCM by **17**, **18** and **19** under similar conditions are shown in Figs. 3–5. At 30 °C, except the polyfunctional "nitro-ester" catalyst **17d** exhibiting excellent performance, the catalytic activities of **17**, **18** and **19** are slightly higher than that of the unmodified **4** using diallylmalonate (Fig. 3) as substrate. All the catalysts, high RCM conversions of **20** (>97%) were achieved after 30 min at 30 °C. In order to clearly compare the efficiencies of the above complexes, they were used in RCM reactions at 0 °C with diallylmalonate (Fig. 4) or diallyltosylamide (Fig. 5) as the substrate. All the ligand modifications resulted in an enhancement in the activity relative to those of the unmodified **4**. The ester catalysts **17a**–**c** and the amide catalysts **18a**,**b** have weak bonding interactions between the carbonyl oxygen and the ruthenium center and they all exhibit very good performance with similar conversions after 6 h. The catalytic activities of the ester catalysts **17a**–**c** are similar to complex **7a** and are lower than complex **10**. It is noteworthy that the polyfunctional "nitro-ester" catalyst **17d** exhibited excellent performance for both substrates and is similar to complex **7b** [12c]. Also of note, is that catalysts **19a** and **19b**, whose carbonyl oxygen ligands do not interact with the metal,

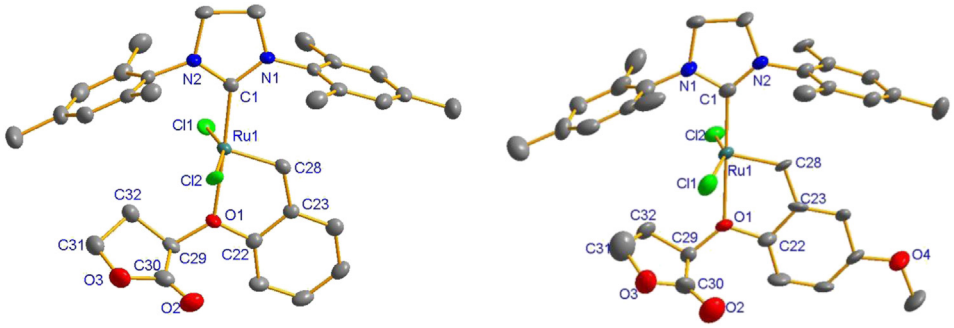


Fig. 2. Perspective view of the catalyst **19a** (left) and **19b** (right). Ellipsoids are drawn at the 50% probability level.

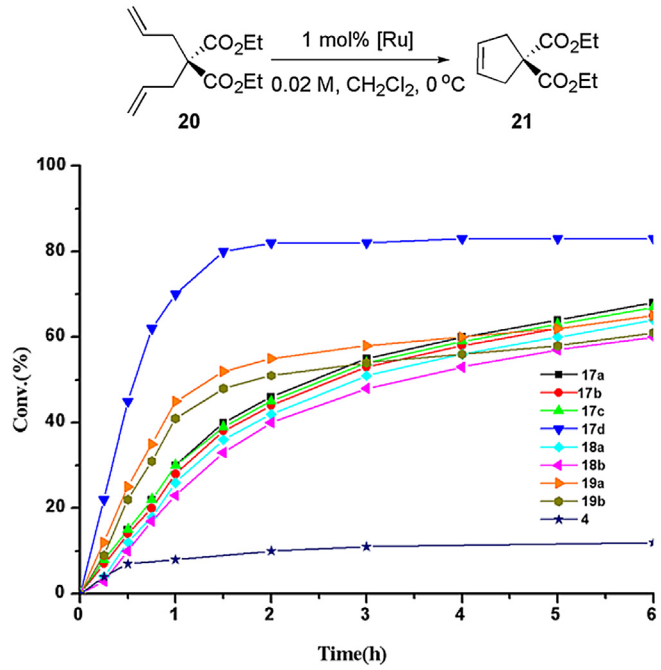


Fig. 4. Catalytic activities of **17**, **18**, **19** and **4** in the RCM of diallyl diethylmalonate (CH_2Cl_2, 1 mol % ruthenium precatalyst), 0 °C, 6 h, conversions calculated from ^1H NMR results.

initiated more rapidly than the others catalysts (except **17d**). So, **17**, **18** and **19** are all highly active RCM catalysts.

Further studies showed that **17**, **18** and **19** are also active for ring closures of substrates with N-protected substrates **22**, **24**, **28**, **30**, **32**, oxygen-containing substrates **38**, **40**, and a sulfur-containing substrate **34** (see Table 3). These reactions resulted in the formation of either five-, six- or seven-membered rings with di- or trisubstituted double bonds. The products were obtained in high conversions at 35 °C with low catalyst loading (0.05–0.5 mol%). For the bulky-substituted dienes **36**, complexes **17**, **18**, **19** all gave low conversions at 35 °C in CH_2Cl_2. However RCM was achieved in good conversions for all catalysts at elevated temperatures (80 °C in toluene) with high catalyst loading (1.0–2.0 mol%) and a longer reaction time (24 h). Cross metathesis of olefins **42** and **43** also produced high yields of new alkene product **44** when 0.05–1.0 mol % of catalyst was used (Table 3, entry 12). Thus, **17**, **18** and **19** are highly active catalysts for a wide range of RCM reactions. They are active with many functional groups which is similar to the behavior of the parent complex **4**.

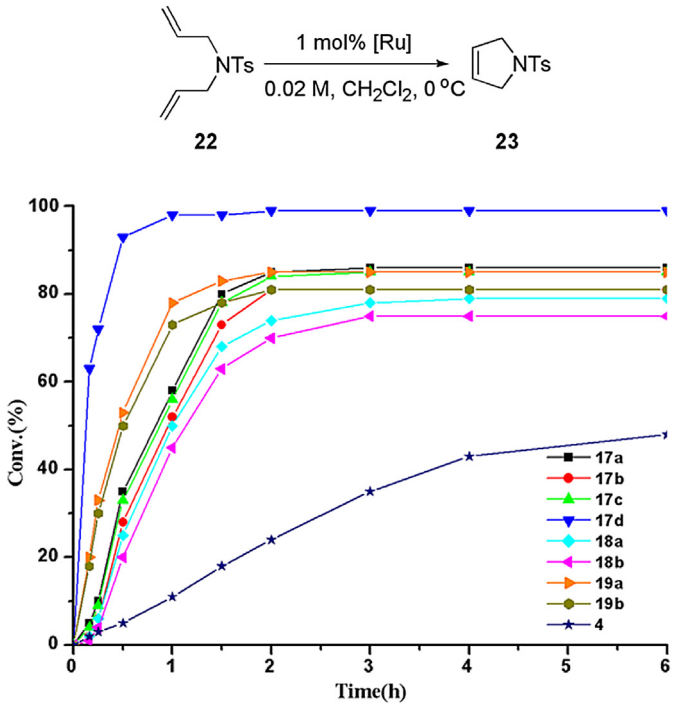


Fig. 5. Catalytic activity of **17**, **18**, **19** and **4** in the RCM of *N*-protected substrate **22** (CH_2Cl_2, 1 mol % ruthenium precatalyst), 0 °C, 6 h, conversions calculated from ^1H NMR results.

3. Conclusions

In order to boost the rate of initiation and the stability of Hoveyda catalysts, a series of new oxygen chelated ruthenium carbene metathesis catalysts containing carbonyl groups were presented. These catalysts have an extra coordinating group (an ester or amide) which gives additional protection to the metal center. Interestingly, all these catalysts were found to exhibit higher activity and stability than the unmodified Hoveyda prototype **4** in RCM and CM reactions for wide range substrates. This work provides a good theoretical basis for the design of new types of olefin metathesis catalysts.

4. Experiment

4.1. General procedure for preparation of *14a–d*

A flask was charged with dry acetone (8 mL), K_2CO_3 (0.5 g, 3.7 mmol) and **13a–d** (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).

4.1.1. Ethyl-2-(2-(prop-1-enyl)phenoxy)propanoate (*14a*)

Colorless oil. Yield: 95.0%. Analytical Data. Calcd (found) for $C_{14}H_{18}O_3$: C, 71.77 (71.56); H, 7.74 (7.78). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.25 (t, J = 6.9 Hz, 3H), 1.63 (d, J = 6.3 Hz, 3H), 1.90 (d, J = 6.7 Hz, 3H), 2.57 (d, J = 6.5 Hz, 3H), 4.19 (dd, J = 13.6 Hz, 6.3 Hz, 2H), 4.70 (dd, J = 13.8 Hz, 6.1 Hz, 1H), 6.18 (m, 1H), 6.70 (m, 2H), 6.87 (m, 1H), 7.04 (m, 1H), 7.38 (d, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 18.8, 19.2, 61.4, 73.6, 113.3, 121.9, 125.7, 126.6, 126.8, 127.7, 130.6, 154.6, 172.4 ppm. IR (KBr) ν: 3065, 2984, 2932, 2852, 1762, 1606, 1486, 1369, 1253, 1217, 1054, 964, 836, 769 cm^{-1}.

4.1.2. Ethyl-2-(4-methoxy-2-(prop-1-enyl)phenoxy)propanoate (*14b*)

Colorless oil. Yield: 94.2%. Analytical Data. Calcd (found) for $C_{15}H_{20}O_4$: C, 68.16 (68.19); H, 7.63 (7.70). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.25 (t, J = 6.8 Hz, 3H), 1.61 (d, J = 6.7 Hz, 3H), 1.91 (q, J = 6.6 Hz, 3H), 3.76 (s, 3H), 4.21 (q, J = 6.7 Hz, 2H), 4.62 (q, J = 7.2 Hz, 1H), 6.18 (m, 1H), 6.64 (m, 3H), 6.96 (d, J = 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 18.8, 19.1, 55.8, 61.3, 74.8, 111.7, 112.8, 115.7, 125.7, 127.1, 129.5, 148.9, 154.7, 172.6 ppm. IR (KBr) ν: 3083, 2986, 2938, 2835, 1751, 1653, 1607, 1584, 1492, 1393, 1376, 1278, 1211, 1096, 1046, 970, 948, 857, 811, 732 cm^{-1}.

Table 3
Application of catalysts **17**, **18** and **19** to different substrates.

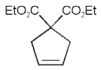
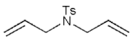
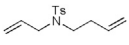
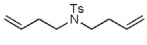
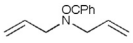
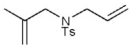
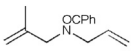
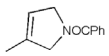
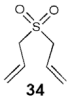
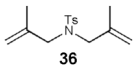
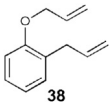
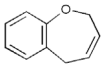
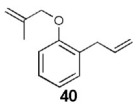
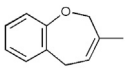
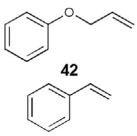
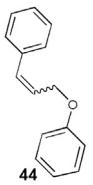
Entry	Diene	Product	Cat. (mol %)	Conditions[a]	Yield (%)[c]
1	 **20**	 **21**	**17a** (0.1)	0.5 h	98
			17b (0.1)	0.5 h	98
			17c (0.1)	0.5 h	97
			17d (0.05)	0.5 h	99
			18a (0.1)	0.5 h	98
			18b (0.1)	0.5 h	97
			19a (0.1)	0.5 h	98
			19b (0.1)	0.5 h	98
2	 **22**	 **23**	**17a** (0.1)	0.5 h	98
			17b (0.1)	0.5 h	98
			17c (0.1)	0.5 h	97
			17d (0.05)	0.5 h	99
			18a (0.1)	0.5 h	98
			18b (0.1)	0.5 h	97
			19a (0.1)	0.5 h	99
			19b (0.1)	0.5 h	98
3	 **24**	 **25**	**17a** (0.1)	0.5 h	98
			17b (0.1)	0.5 h	98
			17c (0.1)	0.5 h	97
			17d (0.05)	0.5 h	98
			18a (0.1)	0.5 h,	98
			18b (0.1)	0.5 h	98
			19a (0.1)	0.5 h	98
			19b (0.1)	0.5 h	98
4	 **26**	 **27**	**17a** (0.1)	0.5 h	98
			17b (0.1)	0.5 h	98
			17c (0.1)	0.5 h	98
			17d (0.05)	0.5 h	99
			18a (0.1)	0.5 h	98
			18b (0.1)	0.5 h	98
			19a (0.1)	0.5 h	98
			19b (0.1)	0.5 h	98
5	 **28**	 **29**	**17a** (0.1)	0.3 h	99
			17b (0.1)	0.3 h	99
			17c (0.1)	0.3 h	98
			17d (0.05)	0.3 h	98
			18a (0.1)	0.3 h	98
			18b (0.1)	0.3 h	98
			19a (0.1)	0.3 h	99
			19b (0.1)	0.3 h	99
6	 **30**	 **31**	**17a** (0.1)	1.0 h	98
			17b (0.1)	1.0 h	98
			17c (0.1)	1.0 h	98
			17d (0.05)	1.0 h	98
			18a (0.1)	1.0 h	98
			18b (0.1)	1.0 h	98
			19a (0.1)	1.0 h	98
			19b (0.1)	1.0 h	98
7	 **32**	 **33**	**17a** (0.1)	0.5 h	98
			17b (0.1)	0.5 h	98
			17c (0.1)	0.5 h	97
			17d (0.05)	0.5 h	98
			18a (0.1)	0.5 h	98
			18b (0.1)	0.5 h	97
			19a (0.1)	0.5 h	98
			19b (0.1)	0.5 h	98
8	 **34**	 **35**	**17a** (0.1)	0.5 h	98
			17b (0.1)	0.5 h	97
			17c (0.1)	0.5 h	97

Table 3 (*continued*)

Entry	Diene	Product	Cat. (mol %)	Conditions[a]	Yield (%)[c]
			17d (0.05)	0.5 h	98
			18a (0.1)	0.5 h	98
			18b (0.1)	0.5 h	97
			19a (0.1)	0.5 h	98
			19b (0.1)	0.5 h	98
9	 **36**	 **37**	**17a** (2.0)	24.0 h[b]	95
			17b (2.0)	24.0 h[b]	94
			17c (2.0)	24.0 h[b]	93
			17d (1.0)	24.0 h[b]	95
			18a (2.0)	24.0 h[b]	95
			18b (2.0)	24.0 h[b]	94
			19a (2.0)	24.0 h[b]	95
			19b (2.0)	24.0 h[b]	94
10	 **38**	 **39**	**17a** (0.1)	0.5 h	98
			17b (0.1)	0.5 h	96
			17c (0.1)	0.5 h	96
			17d (0.05)	0.5 h	98
			18a (0.1)	0.5 h,	98
			18b (0.1)	0.5 h	94
			19a (0.1)	0.5 h	98
			19b (0.1)	0.5 h	97
11	 **40**	 **41**	**17a** (0.5)	12.0 h	97
			17b (0.5)	12.0 h	95
			17c (0.5)	12.0 h	95
			17d (0.05)	12.0 h	97
			18a (0.5)	12.0 h	94
			18b (0.5)	12.0 h	94
			19a (0.5)	12.0 h	96
			19b (0.5)	12.0 h	96
12	 **42** **43**	 **44** Z:E>20:1	**17a** (1.0)	24.0 h	94
			17b (1.0)	24.0 h	94
			17c (1.0)	24.0 h	93
			17d (0.05)	24.0 h	94
			18a (1.0)	24.0 h	93
			18b (1.0)	24.0 h	92
			19a (1.0)	24.0 h	94
			19b (1.0)	24.0 h	93

[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 ^{1}H NMR spectroscopy.

4.1.3. Ethyl-2-(4-nitro-2-(prop-1-enyl)phenoxy)propanoate (**14c**)

Colorless oil. Yield: 92.6%. Analytical Data. Calcd (found) for $C_{14}H_17NO_5$: C, 60.21 (60.19); H, 6.14 (6.17); N, 5.02 (5.05). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.25 (t, J = 7.1 Hz, 3H), 1.71 (d, J = 6.7 Hz, 3H), 1.95 (q, J = 6.5 Hz, 3H), 4.22 (q, J = 7.1 Hz, 2H), 4.85 (q, J = 6.7 Hz, 1H), 6.37 (m, 1H), 6.74 (m, 2H), 8.02 (d, J = 9.0 Hz, 1H), 8.3 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 18.6, 19.1, 61.9, 73.5, 111.914, 122.3, 123.5, 123.9, 128.7, 129.9, 142.2, 158.9, 171.1 ppm. IR (KBr) ν: 3076, 2987, 2940, 2869, 1750, 1653, 1609, 1584, 1516, 1485, 1344, 1255, 1201, 1095, 1049, 967, 816, 746, 657 cm^{-1}.

4.1.4. Ethyl-2-(4-methyl-2-(prop-1-enyl)phenoxy)propanoate (**14d**)

Colorless oil. Yield: 97.7%. Analytical Data. Calcd (found) for $C_{15}H_{20}O_3$: C, 72.55 (72.51); H, 8.12 (8.15). ^{1}H NMR (400 MHz, CDCl3) 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, $CDCl_3$) 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) ν: 3081, 2983, 2936, 2869, 1755, 1637, 1499, 1375, 1272, 1243, 1137, 1096, 1052, 870, 903, 805 cm^{-1}.

4.2. General procedure for preparation of **15a–d**

A flask was charged with **14a–d** (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.

4.2.1. 2-(2-(Prop-1-enyl)phenoxy)propanoic acid (**15a**)

Yellow oil. Yield: 65.1%. Analytical Data. Calcd (found) for $C_{14}H_{19}NO_2$: C, 72.07 (72.12); H, 8.21 (8.17); N, 6.00 (6.09). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.64 (d, J = 6.7 Hz, 3H), 1.90 (d, J = 6.6 Hz, 3H), 2.95 (s, 3H), 3.08 (s, 3H), 4.91 (q, J = 6.6 Hz, 1H), 6.20 (m, 1H), 6.72 (m, 2H), 6.90 (m, 1H), 7.10 (m, 1H), 7.42 (d, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ: 17.6, 18.9, 36.3, 36.5, 74.2, 112.4, 121.4, 125.4, 126.4, 126.5, 127.8, 130.1, 136.9, 153.8, 171.1 ppm. IR (KBr) ν: 3071, 2930, 2917, 1662, 1488, 1455, 1396, 1241, 1115, 1071, 1038, 965, 747 cm^{-1}.

4.2.2. 2-(4-Methoxy-2-(prop-1-enyl)phenoxy)propanoic acid (**15b**)

Yellow oil. Yield: 64.2%. Analytical Data. Calcd (found) for $C_{15}H_{21}NO_3$: C, 68.42 (68.45); H, 8.04 (8.09); N, 5.32 (5.36). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 1.61 (d, J = 6.8 Hz, 3H), 1.92 (d, J = 6.6 Hz, 3H), 2.96 (s, 3H), 3.09 (s, 3H), 3.8 (s, 3H), 4.88 (q, J = 6.7 Hz, 1H), 6.21 (m, 1H), 6.67 (m, 3H), 6.99 (d, J = 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.6, 18.9, 36.3, 36.5, 55.6, 74.8, 111.8, 112.6, 114.3, 125.3, 126.8, 128.6, 148.1, 154.3, 171.4 ppm. IR (KBr) ν: 3080, 2934, 2846, 1660, 1581, 1492, 1428, 1212, 1084, 1039, 965, 915, 814 cm^{-1}.

4.2.3. 2-(4-Methyl-2-(prop-1-enyl)phenoxy)propanoic acid (**15c**)

Light yellow oil. Yield: 67.7%. Analytical Data. Calcd (found) for: $C_{14}H_{18}O_3$ C, 71.77 (71.56); H, 7.74 (7.78) ^{1}H NMR (400 MHz, CDCl3) 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), 6.65–6.68 (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) ν: 3061, 2934, 2933, 1661, 1455, 1444, 1366, 1234, 1110, 1061, 1044, 955, 733 cm^{-1}.

4.3. General procedure for preparation of **16a–d**

A flask was charged with dry acetone (15 mL), K_2CO_3 (0.8 g, 6.0 mmol), 3-bromo-dihydrofuran-2-one (1.0 g, 6.0 mmol) and **13a–d** (4.0 mmol). Then, the reaction mixture was stirred for 4 h under reflux. After cooling to room temperature, the mixture was filtered and concentrated to afford a crude product. The crude product was purified by silica gel chromatography (CH_2Cl_2).

4.3.1. 3-(2-(Prop-1-enyl)phenoxy)-dihydrofuran-2-one (**16a**)

Light yellow oil. Yield: 90.0%. Analytical Data. Calcd (found) for $C_{13}H_{14}O_3$: C, 71.54 (71.48); H, 6.47 (6.42). ^{1}H NMR (400 MHz, CDCl3) 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), 6.95–6.99 (m, 1H), 7.28 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.1, 30.1, 65.6, 73.5, 114.8, 122.8, 125.3, 126.8, 127.4, 128.0, 130.7, 154.1, 173.8 ppm. IR (KBr) ν: 3031, 2997, 2964, 2908, 2874, 1785, 1592, 1485, 1450, 1375, 1239, 1220, 1120, 1018, 993, 948, 753 cm^{-1}.

4.3.2. 3-(4-Methoxy-2-(prop-1-enyl)phenoxy)-dihydrofuran-2-one (**16b**)

Colorless oil. Yield: 88.2%. Analytical Data. Calcd (found) for $C_{13}H_{14}O_3$: C, 71.54 (71.51); H, 6.47 (6.50). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 1.89 (d, J = 5.0 Hz, 3H), 2.68 (m, 1H), 2.75 (m, 1H), 4.39 (m, 1H), 4.45 (m, 1H), 4.91 (q, J = 7.8, 1H), 6.21 (m, 1H), 6.70 (d, J = 10.1, 1H), 6.98 (m, 2H), 7.16 (m, 1H), 7.43 (d, J = 7.7, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.1, 30.1, 55.8, 65.5, 74.8, 11.7, 113.144, 117.57, 125.249, 127.8, 129.8, 148.6, 155.4, 173.9 ppm. IR (KBr) ν: 3037, 2999, 2914, 2836, 1791, 1603, 1583, 1506, 1378, 1290, 1217, 1167, 1097, 1035, 888, 811, 757, 739, 696, 661 cm^{-1}.

4.4. General synthesis of the catalysts

To a Schlenk flask charged with Grubbs' catalyst **2** (0.42 g, 0.50 mmol) and CuCl (0.05 g, 0.50 mmol), compound **14** (or **15**, **16**) (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.

4.4.1. Catalyst **17a**

Yield: 64.1%. Analytical Data. Calcd (found) for $C_{33}H_{40}Cl_2N_2O_3Ru$: C, 57.89 (57.65); H, 5.89 (5.72); N, 4.09 (4.01). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.20 (t, J = 7.1 Hz, 3H), 1.52 (d, J = 6.7, 3H), 2.40 (bs, 6H), 2.50 (bs, 12H), 4.08 (q, J = 7.0 Hz, 2H), 4.14 (s, 4H), 4.98 (q, J = 6.7, 1H), 6.65 (d, J = 8.2 Hz, 1H), 6.92 (m, 2H), 7.06 (s, 4H), 7.48 (t, J = 6.8 Hz, 1H), 16.57 (s, 1H). ^{13}C NMR (100 MHz, CDCl3) δ: 14.1, 17.4, 21.2, 51.7, 62.1, 73.3, 112.5, 122.8, 123.7, 128.8, 129.4, 138.2, 145.8, 151.2, 170.6, 210.4, 299.7 ppm. IR (KBr) ν: 3025, 2918, 2858, 2735, 1938, 1728, 1593, 1574, 1479, 1450, 1410, 1295, 1224, 1115, 1088, 1043, 852, 750, 578 cm^{-1}.

4.4.2. Catalyst **17b**

Yield: 64.2%. Analytical Data. Calcd (found) for $C_34H_{42}Cl_2N_2O_4Ru$: C, 57.14 (57.09); H, 5.92 (5.83); N, 3.92 (3.78). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.22 (t, J = 6.7 Hz, 3H), 1.51 (d, J = 6.6, 3H), 2.41 (bs, 6H), 2.53 (bs, 12H), 3.76 (s, 3H), 4.09 (q, J = 7.0 Hz, 2H), 4.16 (s, 4H), 4.93 (q, J = 6.6, 1H), 6.56 (t, J = 6.8 Hz, 1H), 7.06 (s, 1H), 7.08 (s, 4H), 16.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 17.4, 21.1, 51.7, 55.8, 62.1, 73.3, 107.4, 112.7, 113.8, 129.4, 138.1, 145.3, 146.1, 156.0, 170.8, 210.2, 299.2 ppm. IR (KBr) ν: 3091, 2974, 2916, 2735, 1940, 1724, 1606, 1590, 1488, 1443, 1413, 1306, 1257, 1124, 1087, 1034, 852, 784, 580 cm^{-1}.

4.4.3. Catalyst **17c**

Yield: 62.6%. Analytical Data. Calcd (found) for $C_{33}H_39Cl_2N_3O_5Ru$: C, 54.32 (54.26); H, 5.39 (5.23); N, 5.76 (5.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.21 (t, J = 6.5 Hz, 3H), 1.53 (d, J = 6.3, 3H), 2.43 (bs, 6H), 2.49 (bs, 12H), 4.07 (q, J = 7.1 Hz, 2H), 4.17

(s, 4H), 5.04 (q, $J = 6.7$, 1H), 6.75 (d, $J = 8.9$ Hz, 1H), 7.09 (s, 4H), 7.84 (s, 1H), 8.43 (d, $J = 8.9$ Hz, 1H), 16.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 17.3, 21.1, 51.6, 62.6, 74.5, 112.6, 117.2, 123.4, 129.5, 138.7, 144.2, 145.2, 154.9, 169.8, 207.3, 294.0 ppm. IR (KBr) ν: 3085, 2916, 2738, 1942, 1728, 1605, 1573, 1520, 1479, 1415, 1341, 1263, 1231, 1136, 1089, 1043, 907, 856, 744 cm^{-1}.

4.4.4. Catalyst **17d**

Yield: 67.7%. Analytical Data. Calcd (found) for $C_{34}H_{42}Cl_2N_2O_3Ru$: C, 58.45 (58.29); H, 6.06 (6.01); N, 4.01 (4.05). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.23 (t, $J = 7.1$ Hz, 3H), 1.52 (d, $J = 6.6$, 3H), 2.39 (s, 3H), 2.43 (bs, 6H), 2.53 (bs, 12H), 4.09 (q, $J = 6.7$ Hz, 2H), 4.13 (s, 4H), 4.95 (q, $J = 6.7$, 1H), 6.55 (d, $J = 8.3$ Hz, 1H), 6.76 (s, 4H), 7.10 (s, 4H), 7.30 (d, $J = 8.4$ Hz, 1H), 16.42 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 17.6, 21.4, 27.4, 51.9, 62.3, 73.4, 112.3, 129.5, 129.4, 129.6, 133.1, 138.4, 145.9, 149.5, 171.0, 210.6, 300.1 ppm. IR (KBr) ν: 3034, 2922, 2855, 2735, 1945, 1724, 1486, 1446, 1407, 1257, 1217, 1139, 1103, 1044, 854, 581 cm^{-1}.

4.4.5. Catalyst **18a**

Yield: 66.8%. Analytical Data. Calcd (found) for $C_{33}H_{41}Cl_2N_3O_2Ru$: C, 57.97 (57.60); H, 6.04 (6.10); N, 6.15 (6.08). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.47 (d, $J = 6.4$ Hz, 3H), 2.39 (bs, 6H), 2.51 (bs, 12H), 2.81 (s, 3H), 2.89 (s, 3H), 4.10 (s, 4H), 5.23 (q, $J = 6.6$, 1H), 6.74 (d, $J = 8.0$ Hz, 1H), 6.94 (t, $J = 6.4$ Hz, 2H), 7.06 (s, 4H), 7.48 (t, $J = 6.3$ Hz, 1H), 16.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.8, 21.1, 36.3, 36.9, 51.8, 71.9, 112.8, 122.7, 12.7, 129.3, 137.8, 138.8, 147.1, 151.0, 170.2, 211.1, 302.5 ppm. IR (KBr) ν: 3070, 3033, 2943, 2915, 2735, 1992, 1625, 1477, 1406, 1294, 1258, 1208, 1107, 1040, 852, 749, 508 cm^{-1}.

4.4.6. Catalyst **18b**

Yield: 65.2%. Analytical Data. Calcd (found) for $C_{34}H_{43}Cl_2N_3O_3Ru$: C, 57.22 (57.05); H, 6.07 (6.04); N, 5.89 (5.65). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.38 (d, $J = 6.4$ Hz, 3H), 2.41 (bs, 6H), 2.54 (bs, 12H), 2.75 (s, 3H), 2.77 (s, 3H), 3.77 (s, 3H), 4.10 (s, 4H), 5.22 (q, $J = 6.6$, 1H), 6.50 (s, 1H), 6.76 (d, $J = 8.7$ Hz, 2H), 7.02 (d, $J = 6.3$ Hz, 1H), 7.08 (s, 4H), 16.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.7, 21.1, 36.2, 37.0, 51.7, 60.3, 71.9, 107.0, 113.6, 129.3, 137.7, 138.8, 145.0, 147.5, 156.0, 170.6, 210.9, 301.5 ppm. IR (KBr) ν: 3033, 2918, 2735, 1947, 1634, 1486, 1409, 1259, 1210, 1155, 1097, 1075, 1037, 912, 854, 731, 581 cm^{-1}.

4.4.7. Catalyst **19a**

Yield: 64.0%. Analytical Data. Calcd (found) for $C_{32}H_{36}Cl_2N_2O_3Ru$: C, 57.48 (57.41); H, 5.43 (5.35); N, 4.19 (4.15). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.41 (bs, 6H), 2.45 (bs, 12H), 2.57–2.64 (m, 2H), 4.13 (s, 4H), 4.25–4.30 (m, 1H), 5.15 (q, $J = 6.6$, 1H), 6.91 (m, 2H), 7.07 (d, $J = 7.0$, 4H), 7.28 (s, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 16.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.1, 29.1, 51.5, 65.4, 73.3, 107.0, 114.6, 114.7, 129.4, 138.8, 144.5, 146.0, 156.1, 171.5, 209.6, 294.7 ppm. IR (KBr) ν: 2951, 2917, 2735, 1938, 1785, 1688, 1595, 1574, 1408, 1424, 1398, 1264, 1215, 1175, 1134, 1020, 993, 747, 577 cm^{-1}.

4.4.8. Catalyst **19b**

Yield: 64.2%. Analytical Data. Calcd (found) for $C_{33}H_{38}Cl_2N_2O_4Ru$: C, 56.73 (56.61); H, 5.48 (5.25); N, 4.01 (3.96). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.40 (bs, 6H), 2.45 (bs, 12H), 2.52 (m, 2H), 3.74 (s, 3H), 4.03 (q, $J = 7.4$, 1H), 4.19 (s, 4H), 4.26 (q, $J = 6.6$, 1H), 5.06 (t, $J = 6.84$, 1H), 6.44 (s, 1H), 7.07 (d, $J = 6.8$, 4H), 7.11 (s, 4H), 7.18 (d, $J = 8.9$ Hz, 1H), 16.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.1, 28.9, 51.6, 60.3, 65.4, 73.0, 114.1, 122.5, 124.0, 129.4, 129.7, 138.7, 144.1, 151.7, 171.3, 209.8, 295.5 ppm. IR (KBr) ν: 2916, 2860, 236, 2059, 1950, 1783, 1631, 1604, 1587, 1487, 1422, 1261, 1210, 1175, 1031, 917, 854, 580 cm^{-1}.

4.5. Kinetics study of **17**, **18** and **19**

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 **20** (or diallyltosylamide **22**) 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 ^{1}H NMR methylene proton peaks in the starting material with those in the product. The results are shown in Figs. 3–5.

4.6. Catalytic study of the ruthenium carbenes **17**, **18** and **19**

The general procedure for metathesis reactions with ruthenium carbenes **17**, **18** and **19** was performed as follows: a certain amount of ruthenium carbene catalyst **17** (or **18**, or **19**) (0.0005 mmol) and a solution of the substrate 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 ^{1}H 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 **17**, **18** and **19** for a variety of substrates are shown in Table 3.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.01.017.

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