# A Unique Ruthenium Carbyne Complex: A Highly Thermo-endurable Catalyst for Olefin Metathesis

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**Abstract:** A cationic ruthenium carbyne complex was prepared and was found to initiate olefin metathesis reactions with good activities, which throws a new light on the design of a new type of ruthenium catalyst for RCM reactions. More importantly, no double bond isomerized by-product was observed even at elevated temperatures in reactions catalyzed

## Introduction

Olefin metathesis, especially ring-closing metathesis (RCM), has evolved into an important method for carbon-carbon bond formation in modern organic synthesis.<sup>[1]</sup> Its success has largely relied upon the discovery of the well-defined modern ruthenium catalysts 1 and  $2^{[2]}$  and the parallel development of catalysts 3-8 (Figure 1).<sup>[3]</sup> The repertoire of such catalysts is still expanding<sup>[4]</sup> as exemplified by the recent addition of several ruthenium-based complexes with enhanced catalytic performance, such as 9,<sup>[5a]</sup> 10,<sup>[5b]</sup> and other ruthenium carbene complexes  $[(H_2IMes)Cl_2Ru=CH(PCy_3)]^+[A]^ [A = B(C_6F_5)_4,$ BF<sub>4</sub>, OTf, BPh<sub>4</sub>].<sup>[5c-f]</sup> A carbene ligand coordinated to the ruthenium center is a constituent of the catalysts currently available for olefin metathesis.

These well-defined ruthenium carbene-based olefin metathesis catalysts are generally highly selective for olefin metathesis. However, there has been an increasing number of reports of olefin isomerization when the catalysts were used under harsh reaction conditions, such as high temperature, high dilution, long reaction time, and forced high turnovers.<sup>[6]</sup> The resulting side products are usually difficult to remove *via* standard purification techniques. A large amount of additives, such as 1,4-benzoquinone, and maleic anhydride, has to be added into the reaction system to prevent the undesired isomerization reaction,<sup>[6d]</sup> which brings additional problems for purification of the final products. Hence, it is important to develop

by the new carbyne complex. A mechanism involving the *in situ* conversion of the ruthenium carbyne to a ruthenium carbene complex *via* addition of an iodide to the carbyne carbon was also proposed.

**Keywords:** olefin isomerization; olefin metathesis; ring-closing metathesis; ruthenium carbynes

a catalyst that does not bring about isomerization reaction for the application of olefin metathesis reaction under harsh reaction conditions.

In contrast with the ruthenium carbene complexes, ruthenium carbyne complexes exhibiting catalytic activity towards olefin metathesis are extremely rare and the nature of their catalytic behaviour remains elusive. Although many ruthenium carbyne complexes



Figure 1. Catalysts for olefin metathesis.

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have been prepared,<sup>[7]</sup> only few ruthenium carbyne complexes were reported to catalyze the olefin metathesis reaction. For example, the ring-opening metathesis polymerization (ROMP) of cyclic olefin substrates is catalyzed by a carbyne complex.<sup>[8]</sup> Some of the carbyne complexes are known for catalyzing the dimerization of alkynes rather than for alkyne metathesis.<sup>[7a]</sup> There is a general belief that ruthenium carbyne complexes are inert towards olefin metathesis.<sup>[9]</sup> It is also believed that, to initialize an olefin metathesis reaction, these complexes must be first converted into allenylidene- or alkylidene-ruthenium complexes.<sup>[10]</sup> To the best of our knowledge, none of the ruthenium carbyne complexes synthesized so far has been directly used in ring-closing olefin metathesis.

In this article, we report a stable cationic ruthenium carbyne complex **11** capable of initiating olefin metathesis, including both ring-closing and cross metathesis reactions.

## **Results and Discussion**

The complex **11** was prepared in good yield (>95%) *via* oxidation of **2** with an excess amount of  $I_2$  in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C (Scheme 1).

Unlike its bisphosphine analogues, **11a** and **11b**,<sup>[7a]</sup> the new Ru-carbyne complex does not exist as a neutral, six-coordinate Ru-carbyne structure, which may be due to the large steric effect of the N-heterocarbene preventing the coordination of the iodide ligand to the ruthenium center. The molecular structure of **11** was established by X-ray diffraction (Figure 2).<sup>[11]</sup> The structure reveals the presence of an Ru-carbyne bond with a typical bond length of 1.600 Å, which is in agreement with that of previously reported Ru-carbyne complexes.<sup>[7]</sup>

In sharp contrast to other Ru-carbyne complexes, compound **11** act as an effective catalyst for RCM reactions. The RCM activity of **11** was initially examined using the *N*-protected diallylamine **12** as a test substrate. The kinetic behaviour of RCM of **12** cata-



Scheme 1. Synthesis of ruthenium carbyne complex 11.



**Figure 2.** Molecular structure of the ruthenium carbyne **11** (50% thermal ellipsoid plot; hydrogens have been omitted for clarity; see Supporting Information for details).



**Figure 3.** Kinetic curves for the RCM of diene **12** using **11** as a precatalyst: a) in  $CH_2Cl_2$  at 40°C; b) in the presence of 1.5 mol% Fe in  $CH_2Cl_2$  at 40°C; c) in the presence of 2.5 mol% Fe in  $CH_2Cl_2$  at 40°C; d) in the presence of 5.0 mol% Fe in  $CH_2Cl_2$  at 40°C; e) in toluene at 100°C; f) in the presence of 5.0 mol% Fe in toluene at 100°C. All reactions used 2.5 mol% of **11**. See the Supporting Information for details.

lyzed by **11** (2.5 mol%) under a variety of conditions is illustrated in Figure 3. When  $CH_2Cl_2$  at reflux was used as the solvent (0.10M), the reaction proceeded slowly to give the desired RCM product in low yield (Figure 3, a). Many reagents such as Sn, Fe, Zn, or SnCl<sub>2</sub> were found to increase the reaction rate, and

Table 1. Olefin metathesis reactions catal	yzed by	y Ru-carb	yne com	plex <b>1</b> 1	1
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Entry	Diene	Product	<b>11</b> Ru mol% ( time) <sup>[a]</sup>	Convn. <sup>[b]</sup> (yield [%] )	Entry	Diene	Product	<b>11</b> Ru mol% ( time) <sup>[a]</sup>	Convn. <sup>[b]</sup> (yield [%] )
1	TsN	NTs	1.0% (2 h)	100 (96)	9			1.0% (12 h)	100 (92)
2		13	1.0% (2 h)	100 (96)	10			2.0% (12 h)	98 (91)
3		NTs	1.0% (2 h)	100 (95)	11			1.0% (12 h)	98 (90)
4			1.0% (2 h)	98 (95)	12		35 NTs	1.0% (12 h)	>98 (80)
5	TsN 20	NTs 21	1.0% (3 h)	100 (98)	13	O H PhCN 36		1.0% (12 h)	>98 (86)
6	0 5 22		1.0% (2 h)	100 (95)	14	Ts N 38	NTs 39	2.5% (12 h)	< 5.0
7	O II PhCN 24	O PhCN 25	1.0% (3 h)	100 (96)	15	Ph 0 40	Ph O 42	5.0% (12 h)	95 (93) <i>E</i> only
8	EtOOC EtOOC	COOEt COOEt 27	1.0% (3 h)	100 (96)		Ph 1 41			

<sup>[a]</sup> In toluene(c=1.0 mol/L) at 100 °C in the presence of 5.0 mol% Fe under nitrogen.

<sup>[b]</sup> Conversions were determined by <sup>1</sup>H NMR analysis of the crude reaction mixture, isolated yields were given in parentheses.

among these Fe powder was the best. Thus, the addition of iron powder of up to two equivalents (5.0 mol% relative to the substrate) clearly accelerated the reaction (Figure 3, b–d), which might be due to the role of iron as an efficient scavenger of the  $I_5^$ that is present in the reaction system.<sup>[12]</sup> When the reaction was carried out in toluene (0.10 M) at 100 °C, the catalytic activity of **11** was sharply increased and a complete conversion (>98%) was observed in 40 min (Figure 3, e) and the presence of Fe (5.0 mol%) in the reaction medium, could facilitate complete conversion in 20 min (Figure 3, f).

Further study showed that the catalytic reaction proceeds with better yield on increasing the concentration of substrates to 1.0M. Under these conditions, the RCM of variety of substrates leading to the formation of five-, six-, and seven-membered carbo- and heterocyclic structures with a di- or tri-substituted double bond proceeds cleanly in the presence of 11 (1.0-2.0 mol%) and Fe (5.0 mol%) in toluene at 100°C (entries 1-11, Table 1). The RCM of enyne substrates 34 and 36 also proceeded uneventfully (entries 12 and 13, Table 1). However, only a minimal activity was observed for 11 towards the RCM of structurally more challenging substrates such as the tetrasubstituted diene 38. The complex 11 is also an effective catalyst for typical cross-metathesis reactions (entry 15, Table 1) such as the one between olefins 40 and 41, to give the product 42 E isomer only, indicating 11 as a highly stereoselective catalyst. These studies clearly establish that **11** is an olefin metathesis catalyst with moderate to good activity, and is very comparable with many of the other well known olefin

metathesis catalysts in terms of substrate scope and functional group tolerance.<sup>[13]</sup>

The observation of the unique catalytic activity of ruthenium carbyne to olefins prompted us to do more experiments to uncover the reaction mechanism of 11. This work was started with the attempt to trap any key intermediate by stoichiometric reaction of 11 with styrene, but this failed to reveal any mechanistic implications. Instead styrene was converted to (E)-1,2-diphenylethene quickly and completely, with no key intermediate being observed either during or after the reaction by NMR or TLC, indicating that the key intermediates may be formed in very low concentrations that could not be observed by conventional tools. Further studies showed that the deprivation of  $I_5^-$ , and hence  $I^-$ , by anionic exchange with AgBF<sub>4</sub> completely shuts down the activity of 11. This observation, coupled with the fact that metallic Fe could accelerate the metathesis reaction (vide supra), points to the important role played by I<sup>-</sup>. Based on these preliminary studies on the role of 11 in olefin metathesis, a catalytic mechanism involving the in situ conversion of 11 to the  $\alpha$ -iodobenzylidene complex 44, resulting from the nucleophilic addition of I<sup>-</sup> to either 11 or its resonance structure 43 (Scheme 2) was thus proposed.<sup>[14]</sup> Although addition to carbon-metal triple bonds by heteronucleophiles is well-documented,<sup>[15]</sup> the formation of 44 from 11 represents a rare but potentially general approach for the formation of halocarbene complexes. To further support this mechanistic proposal, a sample of **11** was heated to 100°C in toluene for 30 min and subjected to MS-MS analysis. A signal with m/z = 939.12 corresponding to  $[44-Cl]^+$ (calcd.: m/z = 939.26) was observed, suggesting the formation of 44 as a putative active intermediate. The latter is expected to react with an olefin to generate the 14-electron Ru complex 45 which participates in subsequent catalytic cycles. This hypothesis was further proved by the formation of  $\alpha$ -iodostyrene (de-



**Scheme 2.** Proposed mechanism for the olefin metathesis activity.

tected by GC-MS) in the crude reaction product of the CM of styrene (see the Supporting Information for details). Although the isolation of the key intermediates was unsuccessful, the above mentioned evidence clearly points to the mechanism we proposed.

A comparative study on the behaviour of 11 and several well known catalysts such as 1, 2 and 5 revealed an appealing feature of the Ru-carbyne complex 11: the lack of tendency to bring about double bond isomerization, a cumbersome phenomenon in olefin metathesis by Ru-carbene-based catalysts.<sup>[6]</sup> Although the RCM of tosylamide dienes 12, 14, 16, 20 using the complexes 1, 2, or 5 in CH<sub>2</sub>Cl<sub>2</sub> at room temperature give the desired ring closing products cleanly, it was found that these reactions in toluene at elevated temperature (100°C) resulted in the formation of an undesired secondary product in each case through the isomerization of the initially formed ringclosure product (Table 2, entries 1-4). However, the same reactions proceeded uneventfully with precatalyst 11 under otherwise noted identical conditions with essentially quantitative formation of 13, 15, 17, and 27, without any complication due to the double bond isomerization of the primary products. Additives were used with 2 and 5 to prove the higher selectivity of precatalyst **11**. When 5 mol%  $I_2$  or FeCl<sub>3</sub> was used as the additive with 5, the RCM reaction of diene 12 did not reach completion (86% with  $I_2$ , and only 5% with FeCl<sub>3</sub>). Under similar conditions, when 5 mol% Fe was used with 2 and 5, the isomerization product was detected in a large amount (31% for 2, and 41% for 5). Only FeCl<sub>2</sub> has the tendency to prevent the undesired isomerization reaction (no 13a was observed for 2, and 2% was observed for 5). It is worthy of note that the RCM reaction of 46 in CH<sub>2</sub>Cl<sub>2</sub> at 40°C, using 1, 2, or 5 as catalyst, also resulted in the formation of an undesired product of 47b in significant amounts (Table 2, entry 5). In another example, the RCM reaction of 46 proceeded smoothly using 11 as catalyst in toluene at elevated temperature (100 °C) to give the desired product 47 in good yield (85%) (Table 2, entry 5) without any complication of **47b**. Although the exact mechanism for the prevention of olefin isomerization/migration is unknown at this time, it is highly likely that the released  $I_2$  during the initiation stage of 11 (vide supra) can provide the reaction system with a moderately oxidative atmosphere, and thus may play an important role in eliminating the ruthenium hydride intermediate produced from the decomposition of the ruthenium catalyst while maintaining a low concentration of the in situ generated 14-electron Ru complex 45.<sup>[16]</sup> The formation of the  $Fe^{2+}$  from the released I<sub>2</sub> and the additive Fe may also play an important role in preventing the isomerization reaction (vide supra).

The ability of **11** to prevent olefin isomerization/migration makes it ideally suited for many olefin meta-



Table 2. Cor	nparation of <b>1</b>	1 to 1, 2	, and <b>5</b> f	or different	substrates in mode	el metathesis	reactions a	t elevated to	emperature.
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- <sup>[a]</sup> Except where noted, the catalytic reactions were performed in toluene (c=1.0 mol/L) at 100 °C for 2 h under nitrogen, and in the presence of 5 mol% Fe for **11**.
- <sup>[b]</sup> Determined by <sup>1</sup>H NMR analysis of the crude reaction mixture.
- <sup>[c]</sup> The reaction was conducted in the presence of 5 mol% Fe.
- <sup>[d]</sup> The reaction was conducted in the presence of 5 mol% FeCl<sub>2</sub>.
- <sup>[e]</sup> The reaction was conducted in the presence of 0.5 equiv. benzoquinone.
- <sup>[f]</sup> The reaction was conducted in the presence of  $5 \text{ mol}\% \text{ I}_2$ .
- <sup>[g]</sup> The reaction was conducted in the presence of 5 mol% FeCl<sub>3</sub>.
- <sup>[h]</sup> Conversions were obtained by GC-MS analysis of the crude reaction mixtures.
- <sup>[i]</sup> In CH<sub>2</sub>Cl<sub>2</sub>, at 40 °C for 24 h.
- <sup>[j]</sup>  $c = 1.5 \text{ mmol L}^{-1}$  for **48**, 12 h.
- <sup>[k]</sup> tHE E/Z ratio was obtained by GC-MS analysis of the product.
- <sup>[1]</sup> The conversions were determined by GC-MS.

thesis reactions that require harsh reaction conditions. For example, the RCM of **48** to form the 21-membered macrocyclic lactone **49** was complicated by the formation of a by-product, the 20-membered cyclic lactone **49a**, resulting from an initial isomerization of one of the double bonds in **48** when the Ru-carbene complex **3** was used as the catalyst. Performing the reaction at elevated temperature using toluene as the solvent led to the formation of even more **49a** as reported by Nolan.<sup>[6n]</sup> However, application of catalyst **11** in this reaction in toluene at 100 °C gave **49** in 91% yield without any indication for the formation of **49a** (Table 2, entry 6). Another example for the unique application of **11** was found in the metathetical dimerization of allybenzene **50** (Table 3, entry 1). The use of **2** and **5** as catalysts gave the desired product **51** in low yield (7% for **2**; 33% for **5**) in CH<sub>2</sub>Cl<sub>2</sub> at 40°C, along with the side products 1-[(*E*)-prop-1-enyl]benzene **50a** (22% for **2**; 1% for **5**), (*E*)-1,3-diphenylprop-1-ene **51a** (33% for **2**; 54% for **5**), and (*E*)-1,2diphenylethene **51b** (36% for **2**; 6% for **5**). The use of **1** as the catalyst gave the desired product **51** in higher yield (62%), but the side products 1-[(*E*)-prop-1enyl]benzene **50a** (13%), and the (*E*)-1,3-diphenylprop-1-ene **51a** (11%) were also produced. When 5 mol% **2** and 0.5 equiv. benzoquinone were used as the catalyst, the product **51** was produced in 65% yield in toluene at 100°C for 12 h, along with 2% by-

#### Table 3. CM Reactions of 50, and 52 Catalyzed by 1, 2, 5, and 11.

Entry	Olefin	Cat. (Ru mol%) <sup>[a]</sup> (Conv. in total)	Product (Conv.) <sup>[b]</sup>				
1	Ph		Ph	Ph Ph	Ph	Ph	
	50		50a	51	51a	51b	
		<b>1</b> (5.0) (73%) <sup>[d,e]</sup>	13% ( <i>E</i> only)	62% (4.5:1)	11% ( <i>E</i> only)	0%	
		<b>2</b> (5.0) (98%) <sup>[d,e]</sup>	22% (E only)	7% (4.8:1)	33% ( <i>E</i> only)	36% ( <i>E</i> only)	
		<b>2</b> (5.0) (67%) <sup>[d,g]</sup>	2% ( <i>E</i> only)	65% (2.4:1)	0%	0%	
		<b>5</b> (5.0) (95%) <sup>[d,e]</sup>	1% (E only)	33% (5.6:1)	54% ( <i>E</i> only)	6% ( <i>E</i> only)	
		<b>5</b> (5.0) (79%) <sup>[d,h]</sup>	0%	76% (5.3:1)	3% (E only)	0%	
		<b>5</b> (5.0) (98%) <sup>[d,i]</sup>	25% ( <i>E</i> only)	0%	4% ( <i>E</i> only)	49% ( <i>E</i> only)	
		<b>5</b> (5.0) (98%) <sup>[d,j]</sup>	18% ( <i>E</i> only)	0%	7% ( <i>E</i> only)	49% ( <i>E</i> only)	
		<b>5</b> (5.0) (98%) <sup>[d,k]</sup>	48% ( <i>E</i> only)	21% (3.8:1)	9% ( <i>E</i> only)	1%	
		<b>11</b> (1.0) (79%) <sup>[d,e]</sup>	0%	79% (3.8:1)	0%	0%	
2	Ph N ()7			8 CH3	Ph N Me	My CH3	
	52		Ph	53 Ph		52a	
		<b>1</b> (10.0%) (64%) <sup>[c,d,f]</sup>	5	5% ( <i>E</i> only)	9% (	E only)	
		<b>1</b> (10.0%) (95%) <sup>[d,e,f]</sup>	7	0% ( <i>E</i> only)	25% (	E only)	
		<b>2</b> (10.0%) (90%) <sup>[c,d,f]</sup>	6	5% ( <i>E</i> only)	25% (	E only)	
		<b>2</b> (10.0%) (98%) <sup>[d,e,f]</sup>	5	8% ( <i>E</i> only)	40% (	E only)	
		<b>11</b> (10.0%) (49%) <sup>[d,e,f]</sup>	4	9% ( <i>E</i> only)	0%		
		<b>11</b> (10.0%) (85%) <sup>[d,e,f]</sup>	8	5% ( <i>E</i> only)	0%		

<sup>&</sup>lt;sup>[a]</sup> Except where noted, the reactions were performed toluene (c=1.0 mol/L) at 100°C for 12 h, and in the presence of 5 mol% Fe for 11.

- <sup>[b]</sup> Ratios of the product were obtained by GC for **50**; by isolated yields for **52**.
- <sup>[c]</sup> In CH<sub>2</sub>Cl<sub>2</sub> at 40 °C.
- <sup>[d]</sup> The ratios of Z/E isomer were obtained by GC-MS of the product mixtures.
- <sup>[e]</sup> In xylene at 137 °C.
- <sup>[f]</sup> Only E isomers were detected by <sup>1</sup>H NMR analysis of the product mixtures.
- <sup>[g]</sup> The reaction was conducted in the presence of 0.5 equiv. benzoquinone.
- $^{[h]}\,$  The reaction was conducted in the presence of 5 mol%  $I_2.$
- <sup>[i]</sup> The reaction was conducted in the presence of 5 mol% Fe.
- <sup>[j]</sup> The reaction was conducted in the presence of 5 mol% FeCl<sub>2</sub>.
- <sup>[k]</sup> The reaction was conducted in the presence of 5 mol% FeCl<sub>3</sub>.

product 50a. However benzoquinone produces additional problems for purification of the final product. Under similar conditions, the use of  $5 \mod 12$  and  $I_2$ give the desired product 51 in a yield of 76% along with 3% byproduct **51a**. When 5 mol% Fe or FeCl<sub>2</sub> was used as the additive with 5 mol% 5, there was no product 51 formed. The use of  $5 \mod 8$  FeCl<sub>3</sub> and 5 mol% 5 gave 21% of the desired product 51, along with 48% 50a, 9% 51a, and 23% undefined complexes. In contrast, with 11, the dimerization of 50 proceeded smoothly to give 51 in a higher yield (79%) without any side products. The metathesis of the long-chain terminal olefin 52 to form the symmetric internal olefin 53 was also found to be impaired due to the formation of the internal olefin 52a resulting from double bond migration (Table 3, entry 2). As a result, substrate 52 could not be completely converted to the desired product 53 when the CM reaction was conducted at a lower temperature (40°C) in CH<sub>2</sub>Cl<sub>2</sub> for 12 h, and even under these conditions, a certain amount of undesired 51a (9% for 1; 25% for 2) is formed. Attempts to improve the yield of 53 by carrying out the reaction at a higher reaction temperature (100 °C) in toluene failed and even more of the substrate was converted to 51a (25% for 1; 40% for 2). Again, an improvement in the yield (85%) of the desired product 53 was achieved by the use of 11 when the reaction was performed in xylene at 137 °C, which is because it can be used for a long time at high temperatures

## Conclusions

The cationic complex **11** reported here is the first ruthenium-carbyne compound capable of catalyzing RCM reactions. More importantly, no double bond isomerization by-products were formed even at elevated reaction temperatures in the reactions catalyzed by **11**, indicating the unique applications of **11**. Research on improving the catalytic activity of these types of complexes by varying the substituted groups

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on the phenyl ring as well as the application of **11** in alkyne metathesis is currently underway in our laboratory.

# **Experimental Section**

#### **Preparation of Ruthenium-Carbyne 11**

Ruthenium-carbene complex 2 (100 mg; 118 mmol) and iodine (179 mg; 707 mmol) were added into a flask under N<sub>2</sub>. Dry dichloromethane (8.0 mL) was added into the mixture by syringe under N<sub>2</sub> and the resulting mixture was then stirred for 30 min. After that, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum. The solid was washed with hexane until the hexane layer was colorless. The residue was purified by flash column chromatography on neutral aluminum oxide using CH<sub>2</sub>Cl<sub>2</sub> as eluant to give the desired product 11 as a yellow solid; yield: 166 mg (95%). Anal. found (calcd.) for  $C_{46}H_{64}Cl_2I_5N_2PRu$ : C 37.27 (37.25), H 4.35 (4.36), N 1.89 (1.91); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.90$ – 7.94 (m, 1H, Ph para CH) 7.34-7.42 (m, 4H, Ph ortho CH, meta CH), 4.16 (s, 4H, NCH2CH2N) 6.98 (s, 2H), 6.42 (s, 2H) 2.58 (s, 9H, H<sub>2</sub>Imes CH<sub>3</sub>), 2.45 (s, 6H, H<sub>2</sub>Imes CH<sub>3</sub>), 2.29 (s, 3H, H<sub>2</sub>Imes CH<sub>3</sub>), 1.843, 1.57-1.66, 0.98-1.15 (all m, 33 H, PCy<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 298.05$  (d), 204.2(d, J<sub>C,P</sub>=89.6 Hz), 140.6, 140.2, 138.4, 138.2, 137.0, 136.8, 136.4, 132.1, 130.5, 128.8, 66.2, 54.2 (d,  $J_{CP}$ =3.4 Hz), 52.6, 34.1, 34.0, 29.8, 27.7(d, J<sub>CP</sub>=10.8 Hz), 25.7, 21.5, 21.4, 20.1, 18.6; MS (+ESI): m/z = 847.13, calcd. for [M]<sup>+</sup>: 847.32.

## **General Procedures for the Kinetic Curves of 11**

To a stirred solution of diene **12** (0.80 mmol, 200.4 mg) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) under nitrogen, catalyst **11** (0.02 mmol) was added in a single portion at 40 °C and the reaction mixture was stirred for 7 h at the same temperature. Aliquots (0.20 mL), taken in regular intervals, were quenched immediately with 0.10 mol/L PEI in CH<sub>2</sub>Cl<sub>2</sub>, and then the resultant solution was passed through a short column to remove the Ru metal residue using CH<sub>2</sub>Cl<sub>2</sub> as eluant. Solvent from the collected solution was evaporated under vacuum, and the residue was analyzed by <sup>1</sup>H NMR spectroscopy and the conversion was obtained by comparing the ratios of the integrals of starting materials with those of products. The comparative experiments are presented in Figure 2.

#### **General Procedures for Olefin Metathesis Reactions**

**RCM and enyne metathesis:** A solution of **11** (0.001–0.0025 mmol, 1.00–2.50 mol%), and Fe powder (0.005 mmol, 2.8 mg, 5.0 mol%) was added into a solution of alkene (0.10 mmol) in toluene (0.10 mL, c=1.0 M) under nitrogen. The resulting mixture was stirred at 100 °C for 2–12 h. Then, the solvent was removed under reduced pressure to give a crude product, which was purified by flash chromatography (cyclohexane-CH<sub>2</sub>Cl<sub>2</sub>) to remove the Ru residue. Conversions were obtained from <sup>1</sup>H NMR spectroscopy by comparing the ratios of the integrals of starting materials with those of products. The catalytic activities of ruthenium-carbyne **11** to a variety of substrates are shown in Table 1.

**Cross-metathesis:** To a mixture of alkene (0.10 mmol) and cross-metathesis partner (0.20 mmol) in toluene (0.10 mL, c=1.0 M) was added solid **11** (0.0050 mmol, 5.0 mol%) under nitrogen. The resulting mixture was stirred at 100 °C for 12 h. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (cyclohexane-CH<sub>2</sub>Cl<sub>2</sub>). The catalytic activity of ruthenium carbyne **11** to **40** and **41** is shown in Table 1.

#### **Mechanism Study of 11 for RCM Reactions**

Catalyst **11** (1.0 mmol) was placed into a 5.0-mL roundbottom flask under nitrogen, and toluene (1.0 mL) was transferred at room temperature. The resulting solution was stirred at 100 °C for 0.5 h. Then the reaction mixture was injected to a Thermo Finnigan LCQ Advantage instrument *in situ* to examine the tandem mass spectrometry (MS-MS). The important intermediates such as  $[15-CI]^+$  (calcd: m/z =939.26, found 939.12) and  $[16-H-CI]^+$  (calcd: m/z = 532.13, found 531.02) were observed, see the mass spectra for details.

Catalyst **11** (0.10 mmol) and styrene (1.0 mmol) were placed into a 5-mL round-bottom flask under nitrogen. The flask was evacuated and CHCl<sub>3</sub> (1.0 mL) was transferred at room temperature. The resulting solution was stirred at 40 °C for 1.0 h. After rapidly flash chromatography on silica to remove the catalyst, the reaction mixture was injected to TRACEDSQ GC-mass instrument to detect the reaction intermediates. The (1-iodovinyl)benzene intermediate was observed in the reaction mixture, see the mass spectra for details.

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- [11] CCDC 849386 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.
- [12] It should be noted that most of the added Fe was remained after the catalytic reactions; only very small amount of Fe was converted to FeI<sub>2</sub> even though the Fe was added **2** equivalent to **11**. This may be due to the fact that cleavage of the  $I_5^-$  only happened on the surface of the Fe powder. A significant amount of the released  $I_2$  was always observed during the catalytic reactions.
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- [14] An alternative mechanism, the direct [2+2] addition of 11 with a terminal olefin, would involve the intermediacy of a cationic metallocyclobutane, whose breakdown to form the required propagating species 45 is disfavoured due to the formation of a high energy species, the  $\alpha$ -styrenyl cation:

$$11 \xrightarrow{PCy_3} \begin{bmatrix} H_2 | Mes & H_2 | Mes \\ C |_{\mathcal{A}} & |_{+} & Ph \\ C |_{+$$

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