



# Synthesis of siloxy-modified second generation Hoveyda–Grubbs catalysts and their catalytic activity

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## ABSTRACT

Efficient syntheses of the first ruthenium alkylidene complexes bearing siloxide ligands are described. Second generation Hoveyda–Grubbs catalyst is shown to undergo efficient functionalization with a number of potassium silanulates to give disiloxy derivatives. The complexes obtained are found catalytically active in selected metathesis transformations.

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## 1. Introduction

Transition metal compounds bearing siloxy ligand(s) are of great interest, particularly as models of metal complexes immobilized on silica and silicate surfaces and are known to catalyse a variety of organic reactions [1–3]. More than 100 transition metal complexes bearing terminal or bridging siloxy ligand have been synthesized and structurally and/or spectroscopically characterized for last 25 years [1]. However, information on the application of late TM siloxide complexes in catalysis is scarce [1]. Siloxide complexes, predominantly of early transition metals (Ti, W, Mo) are known to be effectively utilized in molecular catalysis, particularly in polymerization [4], metathesis [5], epoxidation of alkenes [6] and dehydrogenative coupling of silanes [7]. In our group, a number of siloxy complexes of rhodium [8] and iridium [9] have been synthesized and characterized. Moreover, we demonstrated the catalytic activity of these complexes in a number of transformations such as silylative coupling of vinylsilanes with olefins [9a,10], curing of polysiloxanes via hydrosilylation [11], hydroformylation [12] and silylcarbonylation [13] of vinylsilanes as well as hydrogenation and transfer hydrogenation [14]. Recently, we have demonstrated efficient immobilization of rhodium complexes by direct reaction of its siloxy derivative with silica [15]. We expect that it is a general and convenient method of immobilization of late transition metal complexes.

Continuing our interest in synthesis, reactivity and catalytic activity of TM–OSi complexes we started the study of ruthenium siloxide complexes. There is scarce information in literature on ruthenium siloxide complexes [1]. Caulton synthesized siloxide complexes of the type  $[\text{RuH}(\text{OSiR}_3)(\text{CO})(\text{PR}_3)_2]$  (where  $\text{PR}_3 = \text{Pi-Pr}_2\text{Ph}$ ;  $\text{OSiR}_3 = \text{O-SiPh}_3$ ,  $\text{OSiMe}_2\text{Ph}$ ,  $\text{OSiMe}_3$ ) [16],  $[\text{Cp}^*\text{Ru}(\text{PR}_3)(\text{OSiR}_3)]$  and  $[\text{Cp}^*\text{Ru}(\text{PR}_3)(\text{CO})(\text{OSiR}_3)]$  (where  $\text{PR}_3 = \text{Pi-Pr}_2\text{Ph}$ ,  $\text{PCy}_3$ ;  $\text{OSiR}_3 = \text{OSiPh}_3$ ,  $\text{OSiMe}_2\text{Ph}$ ,  $\text{OSiMe}_3$ ) [17] by treatment of the respective ruthenium chloride derivative with potassium silanolate. Siloxy derivative  $[\text{Ru}_3(\text{H})(\mu\text{-OSiEt}_3)(\text{CO})_{10}]$  was obtained with poor yield via a reaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{Et}_3\text{SiOH}$  in the presence of  $[\text{Cp}_2\text{Fe}_2(\text{CO})_4]$  [18]. Siloxysilyl substituted triruthenium clusters have been obtained by interaction of  $\text{HSi}(\text{OSiMe}_3)_3$  and  $\text{HSiMe}(\text{OSiMe}_3)_2$  with  $\text{Ru}_3(\text{CO})_{12}$  [19]. Finally hydrolysis of  $[\{(t\text{-Bu}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}\}\text{Ru}(\text{O-SO}_2\text{CF}_3)]$  led to planar 14e *trans*- $[\text{Ru}(t\text{-Bu}_2\text{PCH}_2\text{SiMe}_2)_2]$  [20]. Catalytic activity of the synthesized complexes has not been examined.

Ruthenium alkylidene complexes of the type proposed by Grubbs, containing two anionic ligands in their structure are very attractive, in particular, in the context of their significant role in catalysis of olefin metathesis.

Herein we report the first examples of ruthenium alkylidene complexes bearing siloxide ligands, based on the second generation Hoveyda–Grubbs catalyst, and demonstrate their catalytic activity in selected metathesis transformations. The choice of the second generation Hoveyda–Grubbs catalyst as a starting material was made on the basis of reports concerning successful exchange of chloride ligands in this complex [see for example Ref. [22]].

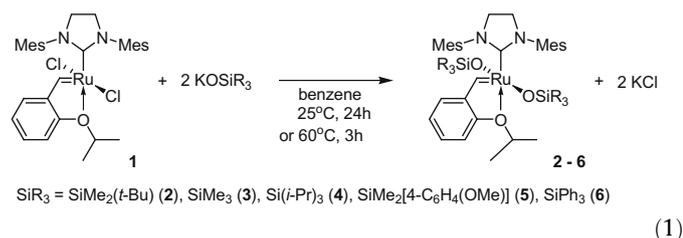
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## 2. Results and discussion

### 2.1. Synthesis

Stirring the benzene solution of the second generation of Hoveyda–Grubbs catalyst (**1**) [21] with two equivalents of potassium dimethyl(*tert*-butyl)silanolate at 60 °C led to gradual change of colour from green to brown. Monitoring of the reaction by <sup>1</sup>H NMR spectroscopy indicated disappearance of the signal at  $\delta = 16.7$  and formation of a new signal at  $\delta = 15.2$  ppm. After 3 h of the reaction course nearly quantitative conversion (98%) of **1** and formation of new alkylidene complex with 95% of NMR yield was observed. Evaporation of the solvent followed by extraction of the product with pentane gave new alkylidene complex whose <sup>1</sup>H and <sup>13</sup>C NMR spectra corresponded to those of the siloxide complex of ruthenium (**2**).



By using the same procedure a series of new siloxy derivatives of the second generation Hoveyda–Grubbs catalyst were synthesized (Eq. (1)). New siloxy complexes were obtained with the NMR yield exceeding 90% for  $\text{SiMe}_2(t\text{-Bu})$ ,  $\text{Si}(i\text{-Pr})_3$ ,  $\text{SiMe}_2[4\text{-C}_6\text{H}_4(\text{OMe})]$ ,  $\text{SiPh}_3$  and 75% for  $\text{SiR}_3 = \text{SiMe}_3$ . However, during the isolation procedure, the relatively good solubility of siloxy complexes in pentane led to reduced isolated yields.

The yields of the complexes formed in the reactions performed in the optimized conditions are given in Table 1. Milder reaction conditions (25 °C) do not lead to higher yields and requires the use of excess amounts of potassium silanolate, whose separation from the complex formed is difficult.

All efforts to synthesise siloxy derivative of the first or second generation Grubbs catalyst failed. Treatment of the catalysts with sodium or potassium silanolates monitored by <sup>1</sup>H NMR resulted in gradual disappearance of the signal of hydrogen at carbene carbon ( $\delta = 20.6$  and 19.6 ppm, respectively). No appearance of new signals in the carbene region of the spectrum was observed.

Precise monitoring of the reaction course revealed the formation of minor amounts (up to 20%) of monosiloxo complex, which seems to be in equilibrium with the starting complex (**1**) and disiloxo derivative. Despite variations in the reaction conditions and stoichiometry no exclusive or predominant formation of monosiloxo derivatives was observed. The highest content of monosiloxo complex (the 2:2:1 molar ratio of **1**, mono- and disiloxo derivative) was detected when **1** was treated with  $\text{KOSiPh}_3$  in benzene at room

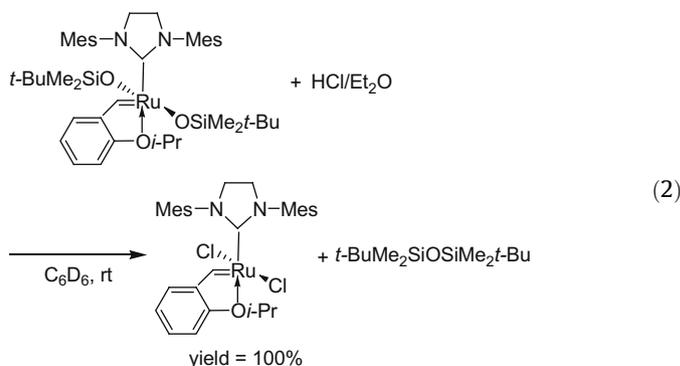
**Table 1**  
Synthesis of ruthenium siloxide alkylidene complexes.

SiR <sub>3</sub>	[Ru]:[KOSiR <sub>3</sub> ]	Temperature (°C)/time (h)	Complex	Isolated yield (%)
SiMe <sub>2</sub> ( <i>t</i> -Bu)	1:2	60/3	<b>2</b>	80
SiMe <sub>3</sub>	1:4	25/24	<b>3</b>	55
SiMe <sub>3</sub>	1:2	60/3	<b>3</b>	60
Si( <i>i</i> -Pr) <sub>3</sub>	1:2	60/3	<b>4</b>	78
SiMe <sub>2</sub> [4-C <sub>6</sub> H <sub>4</sub> (OMe)]	1:2	60/3	<b>5</b>	75
SiPh <sub>3</sub>	1:2	60/3	<b>6</b>	76

temperature. All attempts to isolate the monosubstituted derivative failed. Similar observations were made earlier by Buchmeiser when studying exchange of chlorine ligands with the trifluoroacetate ones [22].

### 2.2. Reactivity

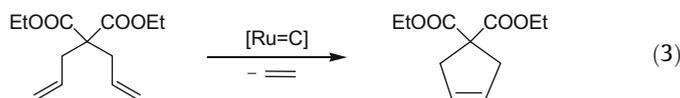
Treatment of benzene solution of siloxy derivative (**2**) with HCl/Et<sub>2</sub>O results in an immediate change in colour from brown to green. Analysis of the reaction mixture by <sup>1</sup>H NMR spectroscopy revealed the quantitative formation of the second generation Hoveyda–Grubbs catalyst (**1**) (Eq. (3)). Similar reactivity of *tert*-butoxy derivative of the first generation catalyst was reported by Grubbs [23]. Titration of C<sub>6</sub>D<sub>6</sub> solution of **2** with etheral solution of HCl in an NMR tube monitored by <sup>1</sup>H NMR revealed gradual disappearance of the signal at 15.2 ppm and appearance of the signal at 16.7 ppm which can be assigned to Hoveyda–Grubbs complex (**1**) (Eq. (2)). Complete exchange of siloxide ligands with the chloride ones was observed after addition of stoichiometric amount of HCl. The reaction was accompanied by the formation of corresponding disiloxane.



Siloxo substituted complexes (**2–6**), unlike the Hoveyda–Grubbs catalyst (**1**), are sensitive to water. However, the solids **2–6** can be stored for weeks in a glove-box without detectable decomposition.

### 2.3. Catalytic activity

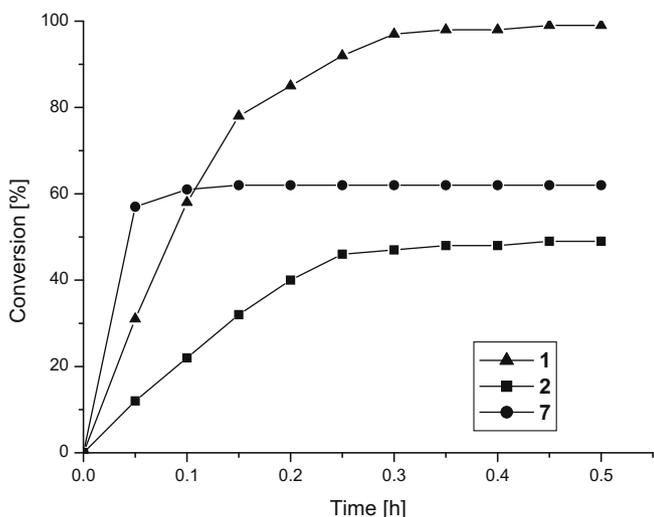
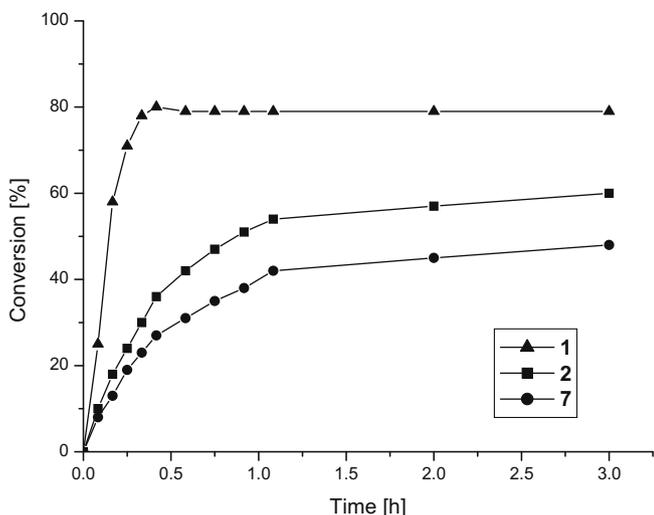
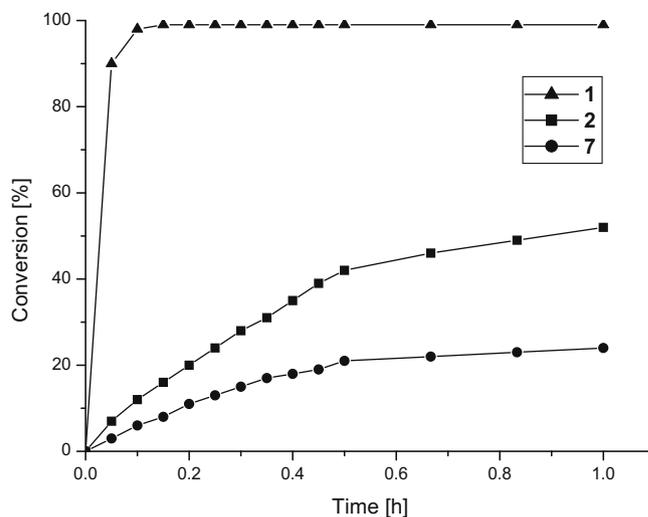
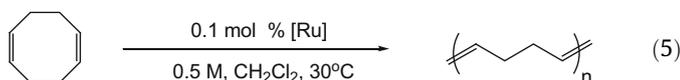
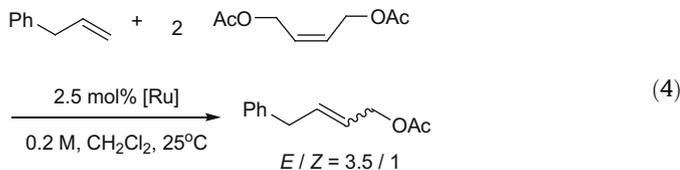
In order to evaluate the catalytic activity of the siloxy complexes (**2–6**) synthesized, preliminary catalytic tests were performed. The results obtained indicated a similar catalytic activity of **2–6** in RCM of diethyl diallyl malonate (Eq. (3)) (Table 2).



Moreover, we performed comparative investigation of relative activity of representative siloxy complex (**2**), second generation Hoveyda–Grubbs catalyst (**1**) and Grubbs first generation catalyst  $[\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})]$  (**7**) in selected model reactions, that is RCM of diethyl diallyl malonate (Eq. (3)) (Fig. 1), CM of *Z*-1,4-diacetoxybutene with allylbenzene (Eq. (4)) (Fig. 2) and ROMP of 1,5-cyclooctadiene (Eq. (5)) (Fig. 3). These results revealed significant decrease in the catalytic activity of disiloxo complex (**2**) in relation to that of the parent Hoveyda–Grubbs catalyst (**1**). In cross-metathesis and ROMP, disiloxo derivatives were found to exhibit higher activity than the first generation Grubbs catalyst. Disappointingly, in RCM of diethyl diallyl malonate, disiloxo complex (**2**) was the least reactive of all the complexes tested.

**Table 2**RCM of diethyl diallyl malonate in the presence of **1** and ruthenium alkylidene siloxides **2–6**.

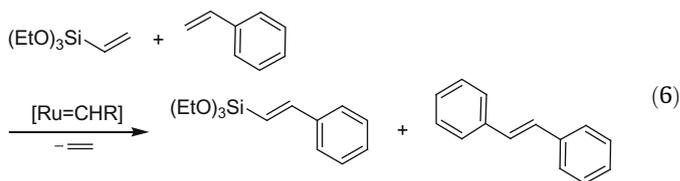
Catalyst	Time (h)	Yield (%)
<b>1</b>	0.5	100
<b>2</b>	2	60
<b>3</b>	2	54
<b>5</b>	2	58
<b>6</b>	2	55

Reactions conditions: CH<sub>2</sub>Cl<sub>2</sub>, reflux, 1 mol% of catalyst.**Fig. 1.** RCM of diethyl diallyl malonate in the presence of **1**, **2** and **7**. Reaction conditions: 1 mol% of catalyst, 0.1 M, CH<sub>2</sub>Cl<sub>2</sub>, 30 °C.**Fig. 2.** CM of Z-1,4-diacetoxybutene with allylbenzene in the presence of **1**, **2** and **7**.**Fig. 3.** ROMP of 1,5-cyclooctadiene in the presence of **1**, **2** and **7**.

These results have shown strongly deactivating effect of siloxy ligands on the catalytic activity of Hoveyda–Grubbs type catalyst in the reactions tested.

The exchange of anionic ligands in the Grubbs type complexes was found to significantly modify the catalytic activity of the complexes. Replacement of chlorine ligands with alkoxy ones, including fluorinated derivatives, in complex **7** brings the disappearance of catalytic activity [22]. On the other hand, Buchmeiser and Nuyken demonstrated that the catalytic activity of Hoveyda–Grubbs catalyst (**1**) is enhanced or preserved by substitution of chlorine with electron-withdrawing ligands [21].

Our results indicate that substitution of chloride ligands in complex **1** with the  $\sigma$ - and  $\pi$ -donor siloxy groups brings about a distinct decrease in the catalytic activity in all reactions tested. However, when ruthenium siloxide (**2**) was used as catalyst in the cross-metathesis of triethoxyvinylsilane with styrene (Eq. (6)) its lower catalytic activity was found advantageous. In the presence of siloxy complex **2**, the reaction led to exclusive and nearly quantitative formation of silylstyrene while the use of **1** resulted in formation of significant amount of the stilbene, the product of competitive homo-metathesis of styrene (Table 3).

**Table 3**CM of styrene with vinyltriethoxysilane in the presence of Hoveyda–Grubbs catalyst (**1**) and selected siloxy derivatives (**2–4**).

Catalyst	Conversion of silane (%)	Yield of silylstyrene (%)	Yield of stilbene (%)
<b>1</b>	100	85 <sup>a</sup>	15 <sup>a</sup>
<b>2</b>	100	96	0
<b>3</b>	100	99	0
<b>4</b>	100	98	0

Reaction conditions: CH<sub>2</sub>Cl<sub>2</sub>, reflux, Ar, cat. 5%, 24 h.<sup>a</sup> 2 h; [H<sub>2</sub>C=CHSi]:[styrene] 1:1.

### 3. Conclusions

Second generation Hoveyda–Grubbs catalyst undergoes exchange of both chloride ligands with the siloxy ones to form siloxy-substituted ruthenium alkylidene complexes, which exhibit catalytic activity in selected olefin transformations. In view of the new method of immobilization of transition metal complexes on silica via interaction of metal siloxy derivative with hydroxy group on silica, the complexes synthesized can be good candidates for direct immobilization on silica.

### 4. Experimental

#### 4.1. General methods and chemicals

All manipulations were carried out under dry argon using standard Schlenk techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Gemini 300 at 300 and 75 MHz, respectively. Mass spectra (FD-MS) were recorded on a Waters Micromass GTC Premier apparatus equipped with FD (Field Desorption) ion source and time of flight analyzer (TOF).

All the chemicals were purchased from Aldrich. Reagent grade pentane, THF and benzene were distilled from sodium/benzophenone under argon. HPLC grade dichloromethane and reagents for catalytic tests were dried prior to use over  $\text{CaH}_2$  and distilled under argon.

#### 4.2. Synthesis of $\text{KOSiMe}_2\text{-t-Bu}$

An oven dried 20 mL Schlenk flask closed with a septum and equipped with a magnetic stirring bar was charged under argon with 0.5 g (12.5 mmol) of KH and 10 mL of dry THF. The suspension of potassium hydride was stirred at room temperature and 0.8 mL (5 mmol) of tertbutyldimethylsilanol was added dropwise to the mixture. Stirring was continued for 24 h at room temp. After this time the THF solution was filtered from the excess of potassium hydride and evaporated to dryness giving potassium silanolate with 98% yield.

#### 4.3. Synthesis of siloxide complexes

##### 4.3.1. $[(\text{H}_2\text{I}Mes)(\text{OSiMe}_2\text{-t-Bu})_2\text{Ru}(\text{=CH-C}_6\text{H}_4(\text{O-}i\text{-Pr-2}))]$ (**2**)

An oven dried 10 mL Schlenk flask equipped with a magnetic stirring bar was charged under argon with 0.05 g ( $8.0 \times 10^{-5}$  mol) of Hoveyda–Grubbs second generation catalyst, 0.027 g ( $1.6 \times 10^{-4}$  mol) of  $\text{KOSiMe}_2\text{-t-Bu}$  and 3 mL of dry benzene. The reaction mixture was stirred and heated in an oil bath at 60 °C for 3 h. The colour change from green to brown and formation of precipitate were observed. After a given reaction time the solvent was evaporated to dryness and the siloxide complex was extracted with 10 mL of dry pentane and filtered from the potassium salt under argon. The solvent was evaporated to dryness giving the ruthenium alkylidene siloxide complex with 80% yield. The other siloxy complexes were synthesized by using similar procedure.

##### 4.3.2. Spectroscopic data

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 15.16 (s, 1H, Ru=CHAr), 7.15–6.80 (m, 3H, aromatic CH), 7.0 (s, 4H, mesityl aromatic CH), 6.37 (d,  $J=8.3$  Hz, 1H, aromatic CH), 4.43 (septet,  $J=6.2$  Hz, 1H,  $(\text{CH}_3)_2\text{CHO}$ ), 3.39 (s, 4H,  $\text{N}(\text{CH}_2)_2\text{N}$ ), 2.52 (s, 12H, mesityl  $o\text{-CH}_3$ ), 2.26 (s, 6H, mesityl  $p\text{-CH}_3$ ), 1.34 (d,  $J=6.2$  Hz, 6H,  $(\text{CH}_3)_2\text{CHO}$ ), 1.04 (s, 18H,  $\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$ ), 0.11 (s, 12H,  $\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 256.2, 219.3, 151.4, 144.9, 138.4, 138.1, 129.6, 129.5, 129.4, 125.2, 122.8, 121.6, 112.7, 73.7, 51.5, 27.7,

26.2, 21.1, 20.8, 18.8,  $-1.0$ ; FD-MS  $[\text{M}]^+$  (not observed); m.p. = 102–104 °C (decomposition).

##### 4.3.3. $[(\text{H}_2\text{I}Mes)(\text{OSiMe}_3)_2\text{Ru}(\text{=CHC}_6\text{H}_4(\text{O-}i\text{-Pr-2}))]$ (**3**)

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 14.99 (s, 1H, Ru=CHAr), 7.15–6.80 (m, 3H, aromatic CH), 7.0 (s, 4H, mesityl aromatic CH), 6.39 (d,  $J=8.1$  Hz, 1H, aromatic CH), 4.39 (septet,  $J=6.2$  Hz, 1H,  $(\text{CH}_3)_2\text{CHO}$ ), 3.41 (s, 4H,  $\text{N}(\text{CH}_2)_2\text{N}$ ), 2.55 (s, 12H, mesityl  $o\text{-CH}_3$ ), 2.27 (s, 6H, mesityl  $p\text{-CH}_3$ ), 1.35 (d,  $J=6.2$  Hz, 6H,  $(\text{CH}_3)_2\text{CHO}$ ), 0.14 (s, 18H,  $\text{OSi}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 255.9, 219.1, 151.2, 144.8, 138.3, 138.1, 129.7, 129.6, 129.5, 125.1, 122.6, 121.4, 112.6, 73.5, 51.4, 26.0, 20.7,  $-1.2$ ; FD-MS  $[\text{M}]^+$ ,  $m/z$  (% intensity): 728.3 (12), 729.3 (7), 730.3 (9), 731.2 (38), 732.2 (50), 733.2 (59), 734.2 (100), 735.2 (40), 736.2 (56), 737.2 (26), 738.2 (7); m.p. = 182–184 °C.

##### 4.3.4. $[(\text{H}_2\text{I}Mes)(\text{OSi}(i\text{-Pr})_3)_2\text{Ru}(\text{=CHC}_6\text{H}_4(\text{O-}i\text{-Pr-2}))]$ (**4**)

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 15.22 (s, 1H, Ru=CHAr), 7.09–6.76 (m, 3H, aromatic CH), 7.0 (s, 4H, mesityl aromatic CH), 6.43 (d,  $J=8.0$  Hz, 1H, aromatic CH), 4.48 (septet,  $J=6.2$  Hz, 1H,  $(\text{CH}_3)_2\text{CHO}$ ), 3.41 (s, 4H,  $\text{N}(\text{CH}_2)_2\text{N}$ ), 2.51 (s, 12H, mesityl  $o\text{-CH}_3$ ), 2.28 (s, 6H, mesityl  $p\text{-CH}_3$ ), 1.33 (d,  $J=6.2$  Hz, 6H,  $(\text{CH}_3)_2\text{CHO}$ ), 1.14 (d,  $J=7.0$  Hz, 36H,  $\text{OSi}(\text{CH}(\text{CH}_3)_2)_3$ ), 1.0 (septet,  $J=7.0$  Hz, 6H,  $\text{OSi}(\text{CH}(\text{CH}_3)_2)_3$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 256.0, 219.8, 151.3, 144.8, 138.3, 129.7, 129.6, 127.3, 125.1, 122.8, 121.5, 113.2, 73.8, 51.4, 21.2, 19.7, 16.2, 14.1; FD-MS  $[\text{M}]^+$ , (not observed); m.p. = 108–110 °C (decomposition).

##### 4.3.5. $[(\text{H}_2\text{I}Mes)(\text{OSiMe}_2(\text{C}_6\text{H}_4\text{OMe-4}))_2\text{Ru}(\text{=CHC}_6\text{H}_4(\text{O-}i\text{-Pr}))]$ (**5**)

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 15.13 (s, 1H, Ru=CHAr), 7.62–7.40 (m, 4H,  $\text{C}_6\text{H}_4\text{OMe}$ ), 7.15–6.87 (m, 4H  $\text{C}_6\text{H}_4\text{OMe}$  and 3H, aromatic CH), 7.03 (s, 4H, mesityl aromatic CH), 6.32 (d,  $J=8.2$  Hz, 1H, aromatic CH), 4.18 (septet,  $J=6.4$  Hz, 1H,  $(\text{CH}_3)_2\text{CHO}$ ), 3.40 (s, 4H,  $\text{N}(\text{CH}_2)_2\text{N}$ ), 3.31 (s, 6H,  $\text{OCH}_3$ ), 2.56 (s, 12H, mesityl  $o\text{-CH}_3$ ), 2.28 (s, 6H, mesityl  $p\text{-CH}_3$ ), 1.36 (d,  $J=6.4$  Hz, 6H,  $(\text{CH}_3)_2\text{CHO}$ ), 0.40 (s, 12H,  $\text{Si}(\text{CH}_3)_2\text{Ar}$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 256.3, 219.5, 161.8, 151.3, 144.8, 138.3, 136.6, 129.6, 129.5, 129.3, 128.0, 126.8, 125.1, 122.9, 121.5, 112.9, 73.7, 51.4, 49.8, 21.8, 21.1, 19.3,  $-0.9$ ; FD-MS  $[\text{M}]^+$ , (not observed); m.p. = 95–98 °C (decomposition).

##### 4.3.6. $[(\text{H}_2\text{I}Mes)(\text{OSiPh}_3)_2\text{Ru}(\text{=CHC}_6\text{H}_4(\text{O-}i\text{-Pr-2}))]$ (**6**)

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 15.57 (s, 1H, Ru=CHAr), 7.68–7.15 (m, 30H,  $\text{OSiPh}_3$ ), 7.13–6.90 (m, 3H, aromatic CH), 7.0 (s, 4H, mesityl aromatic CH), 5.90 (d, 1H,  $J=8.2$  Hz, aromatic CH), 3.85 (septet, 1H,  $J=6.2$  Hz,  $(\text{CH}_3)_2\text{CHO}$ ), 3.35 (s, 4H,  $\text{N}(\text{CH}_2)_2\text{N}$ ), 2.41 (s, 12H, mesityl  $o\text{-CH}_3$ ), 2.33 (s, 6H, mesityl  $p\text{-CH}_3$ ), 1.10 (d,  $J=6.2$  Hz, 6H,  $(\text{CH}_3)_2\text{CHO}$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 259.7, 217.7, 151.6, 144.5, 141.9, 138.4, 136.4, 135.6, 130.0, 129.7, 129.5, 127.9, 126.9, 125.6, 122.4, 121.0, 113.3, 73.9, 51.5, 21.6, 21.2, 19.2; FD-MS  $[\text{M}]^+$ ,  $m/z$  (% intensity): 1100.3 (13), 1101.3 (8), 1102.3 (10), 1103.3 (28), 1104.4 (48), 1105.3 (63), 1106.3 (100), 1107.3 (72), 1108.3 (65), 1109.3 (39), 1110.3 (21), 1111.3 (7); m.p. = 98–100 °C (decomposition).

#### 4.4. Catalytic tests

##### 4.4.1. RCM

An oven dried 3 mL Schlenk flask with a side neck closed with a septum, equipped with a condenser and a magnetic stirring bar was charged under argon with 2.5 mL of  $\text{CH}_2\text{Cl}_2$ , 50  $\mu\text{L}$  of diethyl diallyl malonate ( $2.08 \times 10^{-4}$  mol) and 20  $\mu\text{L}$  of dodecane (internal standard). The mixture was stirred vigorously at 30 °C and 0.0017 g ( $2.08 \times 10^{-6}$  mol) of ruthenium siloxide alkylidene complex was added under argon. A gentle flow of argon was applied. The reaction was monitored by gas chromatography.

#### 4.4.2. Cross-metathesis

An oven dried 3 mL Schlenk flask with a side neck closed with a septum, equipped with a condenser and a magnetic stirring bar was charged under argon with 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub>, 13 μL of allylbenzene (9.75 × 10<sup>-5</sup> mol), 31 μL of Z-1,4-diacetoxy-2-butene (1.95 × 10<sup>-4</sup> mol) and 50 μL of decane (internal standard). The mixture was stirred vigorously at 25 °C and 0.002 g (2.44 × 10<sup>-6</sup> mol) of ruthenium siloxide alkylidene complex was added under argon. A gentle flow of argon was applied. The reaction was monitored by gas chromatography.

#### 4.4.3. ROMP

An oven dried 3 mL Schlenk flask with a side neck closed with a septum, equipped with a condenser and a magnetic stirring bar was charged under argon with 3 mL of CH<sub>2</sub>Cl<sub>2</sub>, 150 μL (1.22 × 10<sup>-3</sup> mol) of 1,5-cyclooctadiene and 50 μL of decane or dodecane (internal standard). The reaction mixture was stirred and heated in an oil bath at 30 °C. Then 0.001 g (1.22 × 10<sup>-6</sup> mol) of ruthenium siloxide alkylidene complex was added under argon. A gentle flow of argon was applied. The reaction was monitored by gas chromatography.

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