Inorganica Chimica Acta xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Note

# Synthesis and characterization of ruthenium(II) complexes with dendritic *N*-heterocyclic carbene ligands

Tetsuaki Fujihara, Takeru Nishida, Jun Terao, Yasushi Tsuji *

*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan*

ARTICLE INFO

*Article history:*
Available online xxxx

*Keywords:*
Ruthenium
*N*-heterocyclic carbene
Dendrimer
Ring-closing metathesis

ABSTRACT

Ru(II) complexes with a *N*-heterocyclic carbene ligand bearing flexible zeroth-, first-, or second-generation dendritic moieties were synthesized and characterized. The structure of the ruthenium complex with the zeroth-generation dendritic moieties was determined by X-ray crystallography. ONIOM calculations showed that the second generation dendritic moieties surrounded the ruthenium core. These complexes worked as active catalysts for the ring-closing metathesis at 25 °C.



## 1. Introduction

Expanding the catalytic surroundings to the nanoscale is of interest, because it may offer new prospects for homogeneous catalysis [1]. We recently developed highly active catalyst systems utilizing steric bulk apart (>1 nm) from a coordination cite [1a,2]. Among them, a 2,3,4,5-tetraphenylphenyl (TPPh) moiety [3] which has rigid and widely spread structure realized extremely active catalytic activity in the Pd-catalyzed air oxidation of alcohol [2g] and for the kinetic resolution of racemic vinyl ethers [2h]. We have also developed ruthenium catalysts bearing *N*-heterocyclic carbene (NHC) ligands [4] with the TPPh moieties. In the ring-closing metathesis (RCM) [6], catalysts bearing the TPPh moieties showed high catalytic activity as compared to that of Grubbs 2nd generation catalyst (Scheme 1) [5].

We are interested in how rigid and flexible frameworks operate in Ru-catalyzed RCM. Here, we have focused on the Fréchet-type poly(benzyl ether) dendrimers [7] as flexible moieties. Dendrimers [8] are particularly interesting frameworks to expand molecular size effectively and systematically. Metallodendrimers, which are dendrimers with organometallic centers, have been extensively investigated, because the well-defined hyperbranched frameworks will bring about unique chemical properties including novel catalysis [9]. We previously prepared a series of Rh complexes with NHC ligands bearing Fréchet-type flexible dendritic frameworks [10]. When the complexes were employed as catalysts in the hydrosilylation of ketones, yields of the corresponding alcohols increased with higher dendrimer generation [10a].

In the present study, we synthesized a series of a series of zeroth- to second-generation dendrimer NHC complexes with a Ru(II) at the core and characterized them. In addition, the dendritic complexes were used as catalysts in RCM. As for metallodendrimer catalysts in the metathesis reactions, there is the only one precedent [11]: a complex with four ruthenium metals located at the periphery of a low generation dendrimer. The complex worked as a recyclable metathesis catalyst, but the dendrimer effect with different generations was not explored. We found that the complexes with the flexible dendritic moieties showed good catalytic activity in RCM.

## 2. Results and discussion

### 2.1. Synthesis and structure of Ru complexes

A series of imidazolium salts bearing Fréchet-type flexible dendrimers ([$G_n$], $n$ = 1, 2, and 3), (**3a–c**), which were precursors for the NHC ligands, were synthesized in four steps (Scheme 2). First, aryl bromides bearing dendritic frameworks (**1a–c**) was synthesized by the reaction of 4-bromo-3,5-dimethylphenol and dendrimer bromides ([$G_n$]-Br: $n$ = 0, 1 and 2) in THF in the presence of $K_2CO_3$ as a base (Scheme 2a). The reaction of **1a–c** with ethylene diamine in the presence of a Pd catalyst with BINAP as the ligand [12] in toluene at 100 °C afforded the corresponding diamines (**2a–c**) in good yields (Scheme 2b). The imidazolium salts (**3a–c**) were obtained by the cyclizing the corresponding diamines with a triethyl orthoformate in the presence of a catalytic amount of acid (Scheme 2c). These new compounds were characterized by elemental analyses, NMR and MALDI-TOF-MS. The reaction of **3a–c** with $(PCy_3)_2(Cl)_2$-Ru=CHPh in the presence of KO*t*Bu followed by treatment with 2-isopropoxystyrene in the presence of CuCl [11] gave the desired ruthenium complexes (**4a–c**) (Scheme 2d). The Grubbs–Hoveyda catalyst bearing IMes (1,3-dimesitylimidazol-2-ylidene) as the

* Corresponding author. Tel.: +81 75 383 2515; fax: +81 75 383 2514.
*E-mail address:* ytsuji@scl.kyoto-u.ac.jp (Y. Tsuji).

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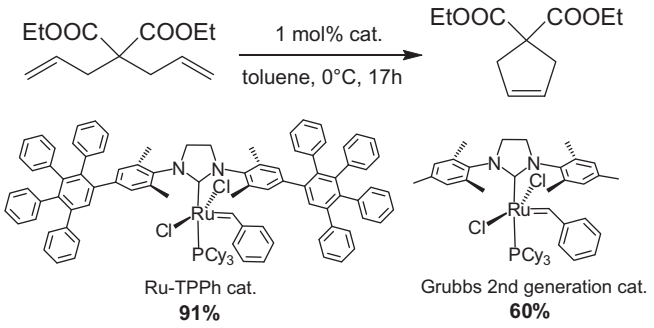
http://dx.doi.org/10.1016/j.ica.2013.05.026




**Scheme 1.** Ruthenium NHC complexes bearing 2,3,4,5-tetraphenylphenyl (TPPh) moieties and its catalytic activity in the ring-closing metathesis.

ligand (**4d**) was also synthesized according to a reported method [11].

The structure of **4a** was successfully determined by the X-ray structural analysis (Fig. 1a). The Ru atom has distorted square pyramidal coordination geometry. The Ru–C (NHC) bond length of **4a** was 1.965(3) Å, which was similar to that of a related ruthenium complex with IMes as the ligand (**4d**: 1.981(5) Å) [11]. Other bond lengths and angles in **4a** were also comparable to those in **4d**. In the solid state the benzyl ether moiety on the NHC ligand (**4a**) spatially spreads out. A single crystal suitable for X-ray crystallographic analysis could not be obtained for **4c**. Therefore, an optimized structure for **4c** (Fig. 1b) was determined by ONIOM calculation [13] (B3LYP/LANL2DZ:UFF) using an initial structure based on the X-ray structure of **4a**. As a result, the dendritic moieties surround the ruthenium center and probably affected its catalytic properties.

### 2.2. Ring-closing metathesis

The catalytic performance of **4a–c** was compared with the Grubbs-Hoveyda catalyst (**4d**) [11] which has methyl groups instead of the benzyl ether moieties. As a probe reaction, RCM of 4,4-diethoxycarbonyl-1,7-octadiene ($c$ = 0.05 M) was carried out in the presence of **4** (1.0 mol%) in toluene (Scheme 3). Employing the zeroth generation catalyst (**4a**), the desired ring-closed products was obtained in 99% yield after 4 h at 25 °C. Higher generation dendritic catalysts, **4b** and **4c**, also showed high catalytic activity, giving the product in 94% and 99% yields, respectively. These yields were comparable with that of **4d**. Thus, the higher flexible dendritic moieties did not affect the catalytic activity. At −30 °C (Scheme 3), the reaction rate decreased and the desired ring-closed products was obtained in 80% yield after 30 h when **4a** was used as a catalyst. Under these reaction conditions, **4a**, **4c** and **4d** gave the product in 75%, 60% and 59% yields, respectively. The yields for **4a–c** decreased as the dendrimer generation increased. In contrast, in the hydrosilylation of ketones catalyzed Rh complexes bearing [$G_0$], [$G_1$] and [$G_2$] moieties, the yields increased with higher dendrimer generation [10a]. Therefore, the dendrimer moieties of metallodendrimers vary considerably to affect catalytic activity.

## 3. Conclusion

In conclusion, novel Ru(II) NHC complexes having flexible dendritic moieties were synthesized and fully characterized. These complexes worked as efficient catalysts in the ring-closing metathesis at 25 °C. Further application of dendritic *N*-heterocyclic carbene ligands in transition-metal-catalyzed reactions are now in progress.

## 4. Experimental

### 4.1. General procedure

All manipulations were performed under an argon atmosphere using standard Schlenk-type glassware on a dual-manifold Schlenk line. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF, $CH_2Cl_2$, and toluene were dried and purified before use by usual methods [14]. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were measured with a JEOL ECX-400P spectrometer. The $^1H$ NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The $^{13}C$ NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC9104. GC analysis was carried out using Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-5, 0.25 mm i.d. × 25 m). Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63–210 μm). Elemental analysis was carried out at Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F254. Fréchet-type dendritic units having a benzyl bromide moiety [$G_n$]-Br ($n$ = 1 and 2) [7,10] and **1a** [15] were prepared according to literature methods.

### 4.2. Synthesis

#### 4.2.1. Synthesis of *1b*

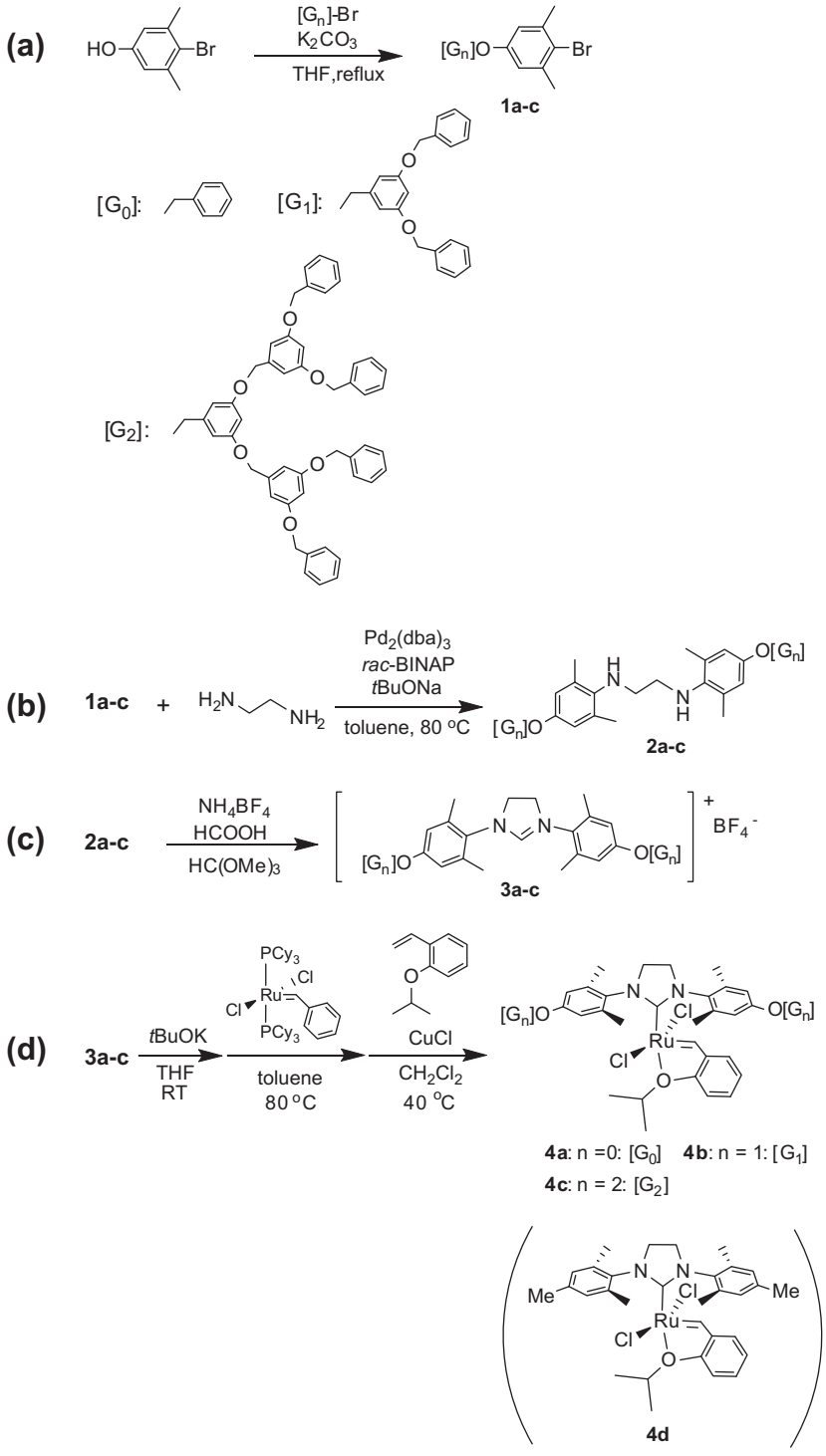
**1b**: [$G_1$]-Br (7.7 g, 20 mmol) was added to a suspension of 4-bromo-3,5-dimethyl phenol (4.0 g, 20 mmol), $K_2CO_3$ (3.3 g, 24 mmol) and 18-crown-6-ether (0.53 g, 2.0 mmol) in THF (60 mL) and the mixture was refluxed for 24 h. After cooling to room temperature, the suspension was filtered through Celite and the filtrate was concentrated to dryness. The residue was separated with silica gel column chromatography using $CH_2Cl_2$ as an eluent. Removal of all volatiles gave white solids. Yield 9.7 g (97%). *Anal.* Calc. for $C_{29}H_{27}BrO_3$: C, 69.19; H, 5.41. Found: C, 69.49; H, 5.43%. $^1H$ NMR (400 Hz, $CDCl_3$): $\delta$ 7.42–7.30 (m, 10H, Ar*H*), 6.69 (s, 2H, Ar*H*), 6.65 (d, $J$ = 2.4 Hz, 2H, Ar*H*), 6.57 (t, $J$ = 2.4 Hz, 1H, Ar*H*), 5.03 (s, 4H, ArC$H_2$), 4.95 (s, 2H, ArC$H_2$), 2.37 (s, 6H, ArC$H_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 160.15, 157.14, 139.32, 139.11, 136.73, 128.57, 128.01, 127.53, 118.55, 114.71, 106.21, 101.51, 70.09, 69.87, 24.07. MALDI-TOF MS (DIT): $m/z$ 503 $[M]^+$.

#### 4.2.2. Synthesis of *1c*

This compound was prepared with [$G_2$]-Br (4.0 g, 5.0 mmol) by the method similar to that used for **1b**. White solids were obtained. Yield 4.3 g (93%). *Anal.* Calc. for $C_{57}H_{51}BrO_7$: C, 73.78; H, 5.54. Found: C, 73.79; H, 5.55%. $^1H$ NMR (400 Hz, $CDCl_3$): $\delta$ 7.42–7.29 (m, 20H, Ar*H*), 6.70 (s, 2H, Ar*H*), 6.67 (d, $J$ = 2.0 Hz, 4H, Ar*H*), 6.64 (d, $J$ = 2.0 Hz, 2H, Ar*H*), 6.57 (t, $J$ = 2.2 Hz, 2H, Ar*H*), 6.54 (t, $J$ = 2.0 Hz, 1H, Ar*H*), 5.03 (s, 8H, ArC$H_2$), 4.97 (s, 4H, ArC$H_2$), 4.94 (s, 2H, ArC$H_2$), 2.36 (s, 6H, ArC$H_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 160.13, 160.02, 157.13, 139.30, 139.17, 139.10 136.71, 128.54, 127.96, 127.51, 118.53, 114.69, 106.34, 106.24, 101.53, 101.47, 70.06, 69.94, 69.85, 24.03. MALDI-TOF MS (DIT): $m/z$ 928 $[M]^+$.

#### 4.2.3. Synthesis of *2a*

A mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.46 g, 0.44 mmol) and *rac*-BINAP (1.1 g, 1.8 mmol) in toluene (500 mL) was stirred for 30 min at room temperature under Ar atmosphere [12]. To this was added ethylene diamine (1.2 mL, 18 mmol), **1a** (10 g, 35 mmol), and NaO*t*Bu (5.1 g, 53 mmol) and the mixture was stirred at 100 °C




**Scheme 2.** Synthesis of a series of ruthenium complexes baring flexible dendritic moieties (**4a**–**c**).

for 24 h under Ar atmosphere. The reaction mixture was filtered with Celite and washed with toluene. The resulting filtrate was concentrated under vacuum. The residue was separated with silica gel column chromatography using $CH_2Cl_2$ as an eluent. Removal of all volatiles gave pale-yellow solids. Yield 4.9 g (57%). *Anal.* Calc. for $C_{32}H_{36}N_2O_2{\cdot}0.5(H_2O)$: C, 78.49; H, 7.62; N, 5.72. Found: C, 78.56; H, 7.36; N, 5.63%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.43–7.29 (m, 10H, Ar*H*), 6.67 (s, 4H, Ar*H*), 4.99 (s, 4H, Ar$CH_2$), 3.09 (s, 4H, NH$CH_2$), 2.30 (s, 12H, Ar$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 154.06, 139.42, 137.43, 131.80, 128.47, 127.76, 127.42, 114.91, 70.12, 49.40, 18.64. MALDI-TOF MS (DIT): *m*/*z* 480 $[M]^+$.

*4.2.4. Synthesis of **2b***

This compound was prepared with **1b** (4.5 g, 8.8 mmol) by the method similar to that used for **2a**. Pale-yellow oil was obtained. Yield 2.5 g (63%). *Anal.* Calc. for $C_{60}H_{60}N_2O_6$: C, 79.62; H, 6.68; N, 3.09. Found: C, 79.66; H, 6.74; N, 3.07%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.43–7.30 (m, 20H, Ar*H*), 6.68 (d, *J* = 2.4 Hz, 4H, Ar*H*), 6.65 (s, 4H, Ar*H*), 6.56 (t, *J* = 2.4 Hz, 2H, Ar*H*), 5.04 (s, 8H, Ar$CH_2$), 4.93 (s, 4H, Ar$CH_2$), 3.09 (s, 4H, NH$CH_2$), 2.30 (s, 12H, Ar$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 160.09, 153.99, 139.94, 139.47, 136.80, 131.80, 128.56, 127.97, 127.54, 114.95, 106.29, 101.39, 70.07, 49.40, 18.66. MALDI-TOF MS (DIT): *m*/*z* 906 $[M]^+$.

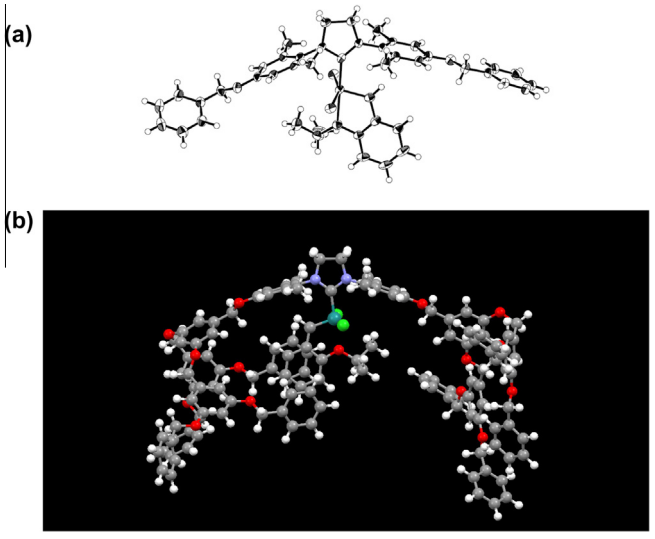
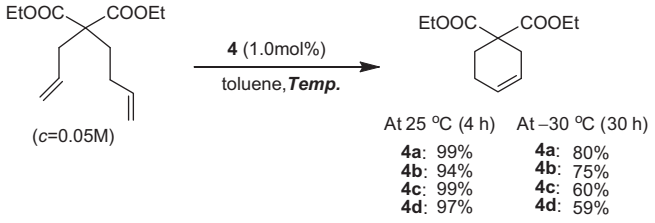



**Fig. 1.** (a) ORTEP drawing of **4a**, and (b) an optimized structure of **4c** calculated by ONIOM method (B3LYP-LANL2DZ:UFF).




**Scheme 3.** Ring-closing metathesis of 4,4-diethoxycarbonyl-1,7-octadiene catalyzed by **4**.

*4.2.5. Synthesis of **2c***

This compound was prepared with **1c** (4.1 g, 4.5 mmol) by the method similar to that used for **2a**. The reaction was carried out for 48 h. Pale-yellow solids were obtained. Yield 2.3 g (70%). *Anal.* Calc. for $C_{116}H_{108}N_2O_{14}$: C, 79.43; H, 6.21; N, 1.60. Found: C, 79.27; H, 6.29; N, 1.61%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.42–7.29 (m, 40H, Ar*H*), 6.68–6.66 (m, 16H, Ar*H*), 6.57 (t, $J$ = 2.0 Hz, 4H, Ar*H*), 6.53 (t, $J$ = 2.2 Hz, 2H, Ar*H*), 5.03 (s, 16H, Ar$CH_2$), 4.97 (s, 8H, Ar$CH_2$), 4.92 (s, 4H, Ar$CH_2$), 3.07 (s, 4H, NH$CH_2$), 2.28 (s, 12H, Ar$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 160.14, 159.99, 154.00, 139.94, 139.48, 139.24, 136.74, 131.82, 128.56, 127.99, 127.55, 114.94, 106.36, 106.34, 101.57, 101.38, 70.09, 69.96, 49.38, 18.66. MALDI-TOF MS (DIT): $m/z$ 1755 $[M]^+$.

*4.2.6. Synthesis of **3a***

Formic acid (0.1 mL) was added to a suspension of **2a** (2.0 g, 4.2 mmol) and $NH_4BF_4$ (0.52 g, 5.0 mmol) in $HC(OEt)_3$ (20 mL). The mixture was refluxed for 3 h under Ar atmosphere. After a removal of all volatiles, the residue was washed with MeOH and dried under vacuum. White solids were obtained. Yield 1.6 g (64%). *Anal.* Calc. for $C_{33}H_{35}BF_4N_2O_2$: C, 68.52; H, 6.10; N, 4.84. Found: C, 68.72; H, 6.14; N, 5.00%. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.09 (s, 1H, NC*H*N), 7.46–7.33 (m, 10H, Ar*H*), 6.86 (s, 4H, Ar*H*), 5.10 (s, 4H, Ar$CH_2$), 4.36 (s, 4H, N($CH_2$)$_2$N), 2.33(s, 12H, Ar$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 160.71, 158.70, 137.27, 136.74, 128.49, 127.92, 127.59, 126.39, 114.81, 69.27, 50.98, 17.50. MALDI-TOF MS (DIT): $m/z$ 491 $[M-BF_4^-]^+$.

*4.2.7. Synthesis of **3b***

Formic acid (0.1 mL) was added to a solution of **2b** (2.4 g, 2.8 mmol) and $NH_4BF_4$ (0.34 g, 3.2 mmol) in $HC(OEt)_3$ (25 mL). The mixture was refluxed for 3 h under Ar atmosphere. After a removal of volatiles under vacuum, the residue was dissolved in $CH_2Cl_2$ and separated with silica gel column chromatography using $CH_2Cl_2$ as an eluent. Removal of all volatiles gave white solids. Yield 1.5 g (55%). *Anal.* Calc. for $C_{61}H_{59}BF_4N_2O_6$: C, 73.05; H, 5.93; N, 2.79. Found: C, 73.32; H, 6.02; N, 2.89. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.81 (s, 1H, NC*H*N), 7.42–7.29 (m, 20H, Ar*H*), 6.71 (s, 4H, Ar*H*), 6.62 (d, $J$ = 2.2 Hz, 4H, Ar*H*), 6.57 (t, $J$ = 2.2 Hz, 2H, Ar*H*), 5.02 (s, 8H, Ar$CH_2$), 4.96 (s, 4H, Ar$CH_2$), 4.47 (s, 4H, N($CH_2$)$_2$N), 2.33 (s, 12H, Ar$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 160.21, 159.48, 159.09, 138.73, 136.95, 136.70, 128.60, 128.04, 127.54, 125.52, 115.31, 106.27, 101.59, 70.11, 69.95, 51.77, 17.93. MALDI-TOF MS (DIT): $m/z$ 916 $[M-BF_4^-]^+$.

*4.2.8. Synthesis of **3c***

This compound was prepared from **2c** (1.8 g, 1.0 mmol) by the similar method used for **3b**. Yield 1.1 g (61%). *Anal.* Calc. for $C_{117}H_{107}BF_4N_2O_{14}$: C, 75.88; H, 5.82; N, 1.51. Found: C, 76.01; H, 5.95; N, 1.69%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62 (s, 1H, NC*H*N), 7.41–7.28 (m, 40H, Ar*H*), 6.71 (s, 4H, Ar*H*), 6.66 (d, $J$ = 2.4 Hz, 8H, Ar*H*), 6.62 (d, $J$ = 2.0 Hz, 4H, Ar*H*), 6.56–6.54 (6H, Ar*H*), 5.01 (s, 18H, Ar$CH_2$), 4.98 (s, 12H, Ar$CH_2$), 4.46 (s, 4H, N($CH_2$)$_2$N), 2.30 (s, 12H, Ar$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 160.15, 160.11, 159.46, 139.20, 138.76, 136.89, 136.73, 128.59, 128.02, 127.53, 125.47, 115.32, 106.33, 106.22, 101.67, 101.56, 70.09, 69.97, 51.74, 17.91. MALDI-TOF MS (DIT): $m/z$ 1765 $[M-BF_4^-]^+$.

*4.2.9. Synthesis of **4a***

A solution of **3a** (0.88 g, 1.5 mmol) in THF (20 mL) was treated with *t*BuOK (1 M THF solution, 1.5 mL, 1.5 mmol) at room temperature under an Ar flow. To the mixture, a solution of Grubbs catalyst 1st generation (0.83 mg, 1.0 mmol) in benzene (20 mL) was transferred via cannula. After stirring at 80 °C for 30 min under Ar atmosphere, all volatiles were removed under vacuum. Then CuCl (0.21 g, 2.1 mmol), 2-isopropoxystylene (0.17 g, 1.0 mmol) and $CH_2Cl_2$ (20 mL) were added to the residue and the resulting suspension was stirred at 40 °C for 1 h. The reaction mixture was concentrated to dryness, and the residue was purified by silica gel column chromatography using pentane/$CH_2Cl_2$ = 1/1 (v/v) as an eluent. Further purification was performed with preparative recycling GPC. Recrystallization from $CH_2Cl_2$/pentane afforded dark green crystals. Yield 0.24 g (29%). *Anal.* Calc. for $C_{43}H_{46}Cl_2N_2O_3Ru$: C, 63.70; H, 5.72; N, 3.45. Found: C, 63.88; H, 5.76; N, 3.43%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 16.65 (s, 1H, Ru=C*H*Ar), 7.50–7.34 (m, 11H, Ar*H*), 6.93–6.78 (m, 13H, Ar*H*), 5.13 (s, 4H, Ar$CH_2$), 4.90 (sept., $J$ = 6.0 Hz, 1H, C*H*($CH_3$)$_2$), 4.14 (s, 4H, N($CH_2$)$_2$N), 2.48 (s, 12H, Ar$CH_3$), 1.29 (d, $J$ = 6.3 Hz, 6H, CH($CH_3$)$_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 297.29, 212.27, 158.76, 152.25, 145.28, 136.99, 129.55, 128.63, 127.97, 127.29, 122.92, 122.28, 114.58, 112.82, 74.97, 69.98, 51.67, 21.11. MALDI-TOF MS (DIT): $m/z$ 811 $[M]^+$.

*4.2.10. Synthesis of **4b***

The complex was prepared with **3b** (0.45 g, 0.15 mmol) by the method similar to that used for **4a**. Dark green solids were obtained. Yield 0.24 g (53%). *Anal.* Calc. for $C_{71}H_{70}Cl_2N_2O_7Ru$: C, 69.03; H, 5.71; N, 2.27. Found: C, 68.92; H, 5.88; N, 2.30%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 16.64 (s, 1H, Ru=C*H*Ar), 7.49–7.31 (m, 21H, Ar*H*), 6.90–6.74 (m, 11H, Ar*H*), 6.60 (t, $J$ = 2.2 Hz, 2H, Ar$CH_2$), 5.06–5.07 (m, 12 H, Ar$CH_2$), 4.85 (sept., $J$ = 6.2 Hz, 1H, C*H*($CH_3$)$_2$), 4.15 (s, 4H, N($CH_2$)$_2$N), 2.47 (s, 12H, Ar$CH_3$), 1.26 (d, $J$ = 6.0 Hz, CH($CH_3$)$_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 297.40, 212.31, 160.22, 158.65, 152.23, 145.27, 139.51, 136.72, 129.56, 128.58, 128.01, 127.58, 122.91, 122.43, 114.62, 112.78, 106.12, 101.45, 74.96, 70.12, 69.98, 51.58, 21.08. MALDI-TOF MS (DIT): $m/z$ 1236 $[M]^+$.

*4.2.11. Synthesis of* ***4c***

The complex was prepared with **3c** (0.81 g, 0.44 mmol) by the method similar to that used for **4a**. Dark green solids were obtained. Yield 0.23 g (30%). *Anal.* Calc. for $C_{127}H_{118}Cl_2N_2O_{15}Ru$: C, 73.18; H, 5.71; N, 1.34. Found: C, 72.89; H, 5.73; N, 1.31%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 16.64 (s, 1H, Ru=C*H*Ar), 7.41–7.29 (m, 41H, Ar*H*), 6.90–6.58 (m, 25H, Ar*H*), 5.06–4.99 (m, 28H, ArC$H_2$), 4.82 (sept., $J$ = 6.0 Hz, 1H, C$H$($CH_3$)$_2$), 4.11 (s, 4H, N($CH_2$)$_2$N), 2.46 (s, 12H, ArC$H_3$), 1.25 (d, $J$ = 6.4 Hz, 6H, CH($CH_3$)$_2$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 297.31, 212.29, 160.15, 158.65, 152.22, 145.26, 139.51, 139.15, 136.73, 129.59, 128.55, 127.97, 127.53, 122.87, 122.40, 114.60, 112.78, 106.41, 106.15, 101.61, 101.43, 74.96, 70.08, 70.01. 69.87, 51.33, 21.09.

*4.3. Procedures for ring-closing metathesis (Scheme 3)*

A ruthenium catalyst **4** (0.0025 mmol, 1.0 mol%), bibenzyl (0.10 mmol, an internal standard), and toluene (5 mL) were placed in a 20 mL Schlenk tube under an Ar flow. After the solution was stirred for 10 min at the temperature (25 or −30 °C), 4,4-diethoxycarbonyl-1,7-octadiene (0.25 mmol) was added *via* a syringe. Then the reaction was carried out at the temperature. After quenching by addition of ethyl vinyl ether to the reaction mixture, a yield of the product was determined by GC analysis (Shimadzu GC 17A, CPB10 column, 25 m length, 0.25 mm i.d.) relative to the internal standard.

*4.4. X-ray crystallography*

Data of **4a** were collected on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71070 Å) at 153 K, and processed using CrystalClear (Rigaku) [16]. The structures were solved by a direct method and refined by full-matrix least-square refinement on $F^2$. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on the calculated positions and not refined. All calculations were performed using the CRYSTALSTRUCTURE software package [17]. *Crystal data for* ***4a***·$CH_2Cl_2$*:* $C_{44}H_{46}N_2O_3Cl_4Ru$, $M$ = 893.74, $T$ = 153 K, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 10.880(2) Å, $b$ = 13.410(2) Å, $c$ = 15.989(3) Å, $\alpha$ = 69.240(8)°, $\beta$ = 81.471(11)°, $\gamma$ = 72.418(10)°, $U$ = 2077.2(7) Å$^3$, $Z$ = 2, $\mu$ (Mo Kα) = 6.759 cm$^{-1}$, Unique reflections 9473 ($R_{int}$ = 0.039), Observed reflections 9473 (all data), $R_1$ = 0.0645 ($I > 2\sigma(I)$), $wR_2$ = 0.1631 (all data). GOF = 1.227.

*4.5. ONIOM calculation*

An optimized structures of **4c** was obtained by ONIOM calculations [13]. In the ONIOM calculation, the molecular system of **4c** was divided into two layers. The high layers were assigned to **4c** with a ruthenium complex core for B3LYP [18]/LANL2DZ [19] calculation. The low layers contain the rest parts of **4c** for molecular mechanics calculation using UFF force field [20]. All calculations were performed with the GAUSSIAN 03 program on a HIT HPC-IA642/SS 1.3/3D-4G.

## Appendix A. Supplementary material

CCDC 786886 contains the supplementary crystallographic data for complex **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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