

Note

## Synthesis of chiral highly hindered cyclopentadienylruthenium compounds

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### Abstract

Optically active highly hindered half-sandwich ruthenium(II) compounds with  $C_2$ -symmetric cyclopentadienyl ligands were synthesized from the ligand precursors, **4** and **5**, which were derived from (–)- $\beta$ -pinene. Thus, the reaction of the ligands with triruthenium dodecacarbonyl produced ruthenium compounds, **10** and **11**, after oxidative treatment. These compounds were characterized by single crystal X-ray crystallography.

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**Keywords:** Chiral ruthenium compound; Half-sandwich complex; Ruthenium dodecacarbonyl

### 1. Introduction

Due to the inherent wealth of chemistry, late transition metals occupy a special place in the arsenal of organic synthesis as their enantiomerically-pure organometallic complexes are useful in a wide range of catalytic or stoichiometric asymmetric reactions [1]. In this regard, enantiopure half-sandwich complexes of late transition metals with homotopic cyclopentadienyl ligands seem to offer many obvious advantages as sources of chirality [2]. The chiral ligand gives rise to chiral induction and fosters the reaction site to one face of the coordination sphere.

However, it is rather surprising to find that these half-sandwich complexes of late transition metal with fused polycyclic  $C_2$ -symmetric cyclopentadienyl ligands have not been prepared. In fact, even though some complexes of Ti and Zr with such backbone have been prepared [3], it is known that, even under vigorous conditions, these cyclopentadienes are extremely resistant to deprotonation [4], which is, unfortunately, the first necessary step toward the synthesis of a variety of the corresponding transition-

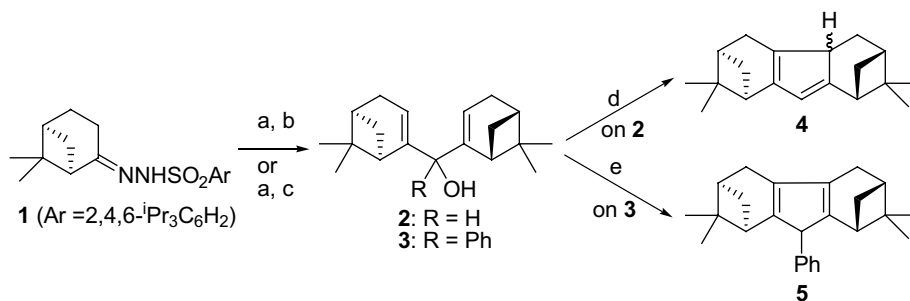
metal complexes. Herein is reported a simple approach toward the synthesis of ruthenium complexes with a  $C_2$ -symmetric cyclopentadienyl ligands, which may be useful chiral catalysts for asymmetric reactions.

### 2. Result and discussion

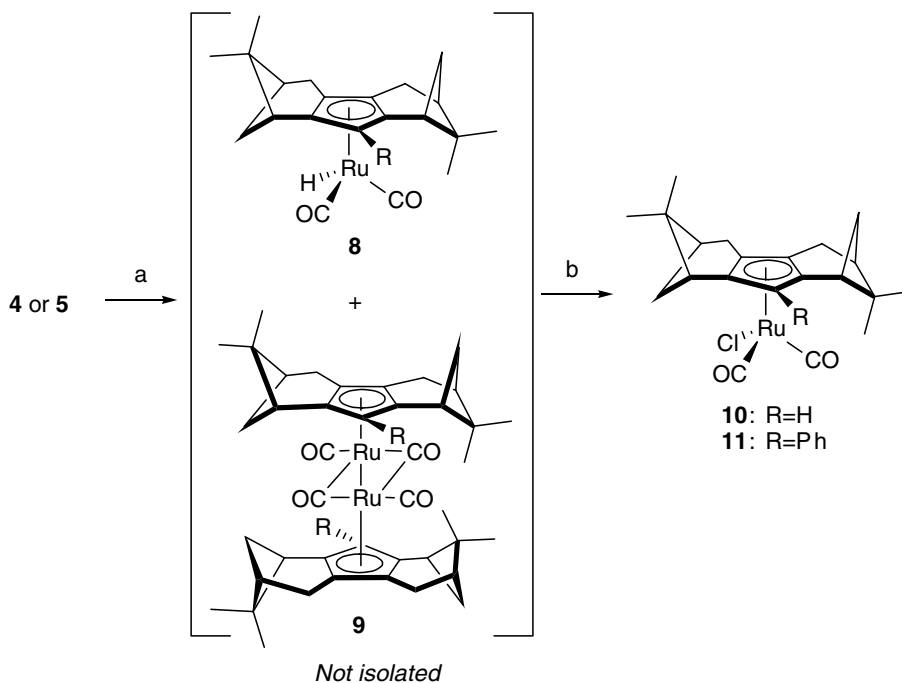
The synthetic scheme of the ligands is illustrated in Scheme 1. The trisylhydrazone **1** [5] of (*IR,5S*)-(+)-nopione, which is available through ozonolysis of (–)- $\beta$ -pinene (~80%) [6], was treated with 2.2 equiv. of *sec*-butyllithium in THF at –78 °C under the standard Shapiro reaction condition [7]. After warming to 0 °C, the resulting vinylolithium species was treated with 0.5 equiv. of ethyl formate or benzoyl chloride at –78 °C to give the corresponding divinyl carbinols **2** and **3** in 70% and 74% yields, respectively. The subsequent standard Nazarov electrocyclization [8] of the unsubstituted alcohol **2**, using a catalytic amount (6 mol%) of concentrated sulfuric acid in THF, gave a 69% yield of a mixture of the chirally annulated cyclopentadiene isomers, among which the less substituted ones with a  $sp^3$  carbon at the ring junction, **4**, were the major isomers with a *ca.* 1:1.3 ratio, as determined by  $^1\text{H}$  NMR spectroscopy (Scheme 1).

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Scheme 1. Synthetic scheme of the ligands **4** and **5**: (a) *sec*-BuLi (2.2 equiv.), THF,  $-78 \rightarrow 0^\circ\text{C}$ , 2 h; (b) HCO<sub>2</sub>Et (0.5 equiv.),  $-78^\circ\text{C} \rightarrow \text{rt}$ , 12 h, 70%; (c) PhCOCl (0.5 equiv.),  $-78^\circ\text{C} \rightarrow \text{rt}$ , 12 h, 74%; (d) H<sub>2</sub>SO<sub>4</sub> (0.06 equiv.), THF, rt, 1 h, 69% (dr = *ca.* ~1:1.3); and (e) BF<sub>3</sub>•OEt<sub>2</sub> (2.0 equiv.), Et<sub>2</sub>O,  $0^\circ\text{C}$ , 5 h, 60%.



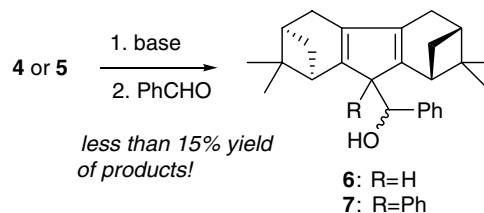
Scheme 2. Complexation scheme of ligands **4** and **5**: (a) Ru<sub>3</sub>(CO)<sub>12</sub>, *n*-decane,  $160^\circ\text{C}$ , 3–12 h and (b) O<sub>2</sub>, HCl, EtOH, CHCl<sub>3</sub>, 4 h, 33–35%.

On the other hand, for the phenyl-substituted carbinol **3**, boron trifluoride diethyl etherate among many acids examined furnished a 60% yield of the Nazarov product **5**, which had a different ring junction from the reaction product **4** derived from the unsubstituted alcohol **2** (Scheme 1).

Various attempts to introduce ruthenium moieties into the chiral cyclopentadienes were largely unsuccessful. The chiral cyclopentadienes were acid-sensitive and rapidly turned black even on mild heating, which precluded the direct interaction with various forms of ruthenium trichloride [9]. Additionally, the severe steric hindrance of the cyclopentadienes may be another major contributing factor against the complexation with ruthenium trichloride.

Because of these difficulties, basic reaction conditions were examined. The cyclopentadienide anions, derived from the deprotonation of the chiral cyclopentadienes **4**

and **5** [10], were quenched with benzaldehyde to provide the corresponding adducts **6** and **7** in a less than 15% yields. The corresponding reaction of the anions with various forms of ruthenium trichloride did not yield any trace of the cyclopentadienylruthenium species.



Consequently, the cyclopentadiene **4** was treated with triruthenium dodecacarbonyl at  $160^\circ\text{C}$  in *n*-decane under neutral conditions [11]. The resulting mixture of the

ruthenium(II) hydride **8** and the ruthenium(I) dimer **9** species (*vide infra*) was treated with HCl and O<sub>2</sub> in CHCl<sub>3</sub> [12] to furnish the desired complex **10** after column chromatography and subsequent recrystallization from *n*-hexane (Scheme 2). Yield of the purified complex was only moderate (~33%), presumably due to the steric congestion of the annulated chiral cyclopentadiene. For the chiral cyclopentadienylruthenium complex **10**, the cyclopentadienyl pro-

ton was observed as a singlet at  $\delta$  4.12 (in CDCl<sub>3</sub>) in <sup>1</sup>H NMR spectrum, and its IR spectrum in the carbonyl region showed two sharp carbonyl stretches at 2028 and 1967 cm<sup>-1</sup>. The electrospray ionization-time of flight (ESI-TOF) mass spectrum showed the base peak of  $m/z = 411.0906$  (calcd. 411.0898), which represents fragment species resulting from removal of a chloride ion from molecular ion.

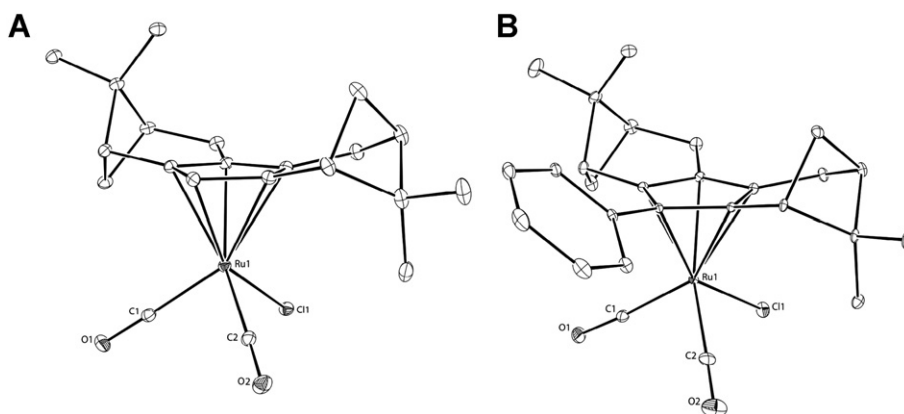


Fig. 1. X-ray crystal structure of chiral cyclopentadienylruthenium compounds **10** (A) and **11** (B). Hydrogen atoms have been omitted for clarity.

Table 1  
Crystal data and structure refinement detail for **10** and **11**

	<b>10</b>	<b>11</b>
Empirical formula	RuC <sub>21</sub> H <sub>25</sub> ClO <sub>2</sub>	RuC <sub>27</sub> H <sub>29</sub> ClO <sub>2</sub>
Formula weight	445.93	522.02
Temperature (K)	173(2)	100(2)
Wavelength (Å)	0.71073	0.70000
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	12.5422(14)	10.390(2)
<i>b</i> (Å)	20.214(2)	13.342(3)
<i>c</i> (Å)	7.7384(9)	16.966(3)
$\alpha$ (°)	90	90
$\beta$ (°)	90	90
$\gamma$ (°)	90	90
Volume (Å <sup>3</sup> )	1961.9(4)	2351.9(8)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.510	1.474
Absorption coefficient (mm <sup>-1</sup> )	0.946	0.801
<i>F</i> (000)	912	1072
Crystal size (mm)	0.70 × 0.50 × 0.20	0.15 × 0.05 × 0.05
Theta range for data collection (°)	1.91–28.32	1.91–30.37
Index ranges	−16 ≤ <i>h</i> ≤ 15, −25 ≤ <i>k</i> ≤ 26, −10 ≤ <i>l</i> ≤ 7	0 ≤ <i>h</i> ≤ 15, −19 ≤ <i>k</i> ≤ 19, −23 ≤ <i>l</i> ≤ 24
Reflections collected	12590	13444
Independent reflections [ <i>R</i> <sub>int</sub> ]	4728 [0.0188]	7356 [0.0453]
Completeness	98.6% (theta = 28.32°)	99.2% (theta = 30.37°)
Absorption correction	Semi-empirical from equivalents	Empirical
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4728/0/326	7356/0/396
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.064	1.030
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0190, <i>wR</i> <sub>2</sub> = 0.0453	<i>R</i> <sub>1</sub> = 0.0267, <i>wR</i> <sub>2</sub> = 0.0707
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0197, <i>wR</i> <sub>2</sub> = 0.0456	<i>R</i> <sub>1</sub> = 0.0273, <i>wR</i> <sub>2</sub> = 0.0709
Absolute structure parameter	−0.012(19)	0.00
Largest difference in peak and hole	0.617 and −0.316 e Å <sup>-3</sup>	0.532 and −0.951 e Å <sup>-3</sup>

In these reactions, the initial products **8** or **9** ( $R = H$ ) were unstable and thus could not be isolated, but their presence was qualitatively judged by the analysis of the initial reaction mixtures by FT-IR and  $^1H$  NMR: The band at 1940 and  $1773\text{ cm}^{-1}$  in the FT-IR spectrum are due to the dimer **9** and the peak at  $\delta$  -10 ppm in the  $^1H$  NMR are from the hydride **8**. In the same manner, the cyclopentadiene **5** was converted more cleanly to the desired phenylated complex **11** in 35% yield. (Scheme 2).

Fig. 1 and Table 1 illustrates the crystal structures of the complexes determined by X-ray crystallography. Interestingly, both of the complexes, **10** and **11**, with the  $C_2$  symmetric cyclopentadienyl ligands have all of the carbonyl ligands away from the two adjacent bicycle moieties. In the case phenyl-substituted complex **11**, the phenyl group attached on the cyclopentadienyl core bisects the cyclopentadienyl plane by  $42.6^\circ$ , which may be expected to provide a more effective asymmetric environment as a catalyst.

In summary, new chiral ruthenium complexes with  $C_2$ -symmetric cyclopentadienyl ligands were synthesized and characterized. Work is underway to utilize these compounds as asymmetric catalysts in organic synthesis.

### 3. Experimental

#### 3.1. General methods

All the reactions were carried out under dry and inert atmosphere in flame-dried glassware unless otherwise indicated. Tetrahydrofuran and diethyl ether were freshly dried by sodium-benzophenone ketyl under nitrogen atmosphere prior to use. Other solvents were dried by calcium hydride or other standard drying methods. *sec*-Butyllithium was standardized by titration with *N*-benzylbenzamide as indicator. Flash column chromatography was carried out on silica gel 60 (merck) unless otherwise indicated.  $^1H$  and  $^{13}C$  NMR spectra were recorded at 500 or 300 MHz and at 125.7 or 75.5 MHz, respectively (500 MHz: Varian Inova-500, 300 MHz: Varian Gemini-300BB). Chemical shifts are reported in ppm using the solvent residual peak as internal standard. GC–Mass spectra (Agilent 5973N) and Microanalyses (Flash EA1112) were provided from Organic Chemistry Reaction Center at the Sogang University. Infrared spectra were obtained on a Nicolet Avatar FT-IR spectrometer. ESI-TOF-MS spectra were obtained on Waters LCT/KC434 ESI-TOF mass spectrometer.

#### 3.2. Preparation of (1*R*,5*S*)-nopinone trisylhydrazone (**1**)

To a solution of 2,4,6-triisopropylbenzenesulfonylhydrazine (25.5 g, 85.4 mmol) in acetonitrile (40 mL) were added (1*R*,5*S*)-(+)-nopinone (10.8 mL, 76.7 mmol) and concentrated HCl (7.5 mL). The reaction mixture was

stirred for 24 h, during which period white solids precipitated. The reaction mixture was cooled to  $-20^\circ\text{C}$  for 12 h and the solid was filtered by filtration. The mother liquor was concentrated at reduced pressure, and, after addition of dichloromethane, the organic layer was washed with saturated sodium bicarbonate. The combined organic layer was dried over anhydrous sodium sulfate. After removal of solvents, additional solid product was collected. The combined solids were dissolved in dichloromethane and filtered to remove a small amount of insoluble solids. After removal of solvent, the pure hydrazone **1** was obtained as white solid. (23.8 g, 65%).

$^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.15 (s, 2H), 4.22 (heptet,  $J = 6.9$  Hz, 2H), 2.89 (heptet,  $J = 6.9$  Hz, 1H), 2.55 (t,  $J = 5.4$  Hz, 1H), 2.20–2.45 (m, 3H), 1.75–2.10 (m, 4H), 1.21–1.31 (m, 21H), 0.59 (s, 3H).

$^{13}C$  NMR (75.5 MHz,  $CDCl_3$ )  $\delta$  163.85, 153.04, 151.39, 131.67, 123.75, 51.24, 40.58, 40.30, 34.27, 29.94, 27.36, 25.66, 24.97, 24.89, 23.69, 23.65, 22.27, 21.95, 19.86.

ESI-TOF-MS (relative abundance):  $m/z = 441.2543$  (100)  $[M + Na]^+$ , Calc. for  $[M + Na]^+$ : 441.2552.

Anal. Calc. for  $C_{24}H_{38}N_2O_2S$ : C, 68.86; H, 9.15; N, 6.69; S, 7.66. Found: C, 68.89; H, 9.10; N, 6.64; S, 7.65%.

#### 3.3. Preparation of bis[(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]methanol (**2**)

To a solution of the hydrazone **1** (12.0 g, 28.7 mmol) in dry THF (80 mL) at  $-78^\circ\text{C}$ , 1.4 M *sec*-butyllithium solution in cyclohexane (45.1 mL, 63.1 mmol) was added dropwise over a period of 15 min. The reaction mixture was stirred at  $-78^\circ\text{C}$  for 2 h, and at  $0^\circ\text{C}$  for 20 min. To the reaction mixture at  $-78^\circ\text{C}$ , a solution of ethyl formate (1.16 mL, 14.4 mmol) in dry THF (4 mL) was added dropwise over 10 min. After the addition, the reaction mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of water, and the resulting mixture was concentrated *in vacuo*, and then extracted with *n*-hexane. The combined organic layer was dried over anhydrous sodium sulfate and, after filtration, concentrated under reduced pressure. The remained residue was purified by column chromatography (eluted with 5% ethyl acetate in *n*-hexane) to give **2** as a white solid (2.75 g, 70%).

$^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  5.52 (m, 1H), 5.47 (s, 1H), 4.30 (s, 1H), 1.95–2.39 (m, 10H), 1.38 (d,  $J = 3.9$  Hz, 1H), 1.28 (s, 3H), 1.26 (s, 3H), 0.99–1.04 (partially overlapped d,  $J = 8.4$  Hz, 2H), 0.86 (s, 3H), 0.85 (s, 3H).

$^{13}C$  NMR (75.5 MHz,  $CDCl_3$ )  $\delta$  148.10, 147.76, 121.11, 116.08, 77.37, 43.48, 41.39, 41.08, 40.93, 37.96, 37.71, 31.89, 31.81, 31.45, 31.25, 26.39, 26.20, 21.53, 21.21.

MS (EI)  $M^+ = 272$ , Calc. = 272.43.

Anal. Calc. for  $C_{19}H_{28}O$ : C, 83.77; H, 10.36. Found: C, 83.59; H, 10.48%.

### 3.4. Preparation of bis[(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]phenylmethanol (**3**)

The phenylated alcohol **3** was prepared by same method as the preparation of the secondary alcohol **2** except for the use of benzoyl chloride. The alcohol **3** was obtained in 74% yield as white solid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25–7.39 (m, 5H), 5.57 (m, 1H), 4.94 (m, 1H), 2.50–2.02 (m, 10H), 1.74 (s, 1H), 1.29 (s, 3H), 1.20–1.17 (m, 5H), 0.90 (s, 3H), 0.69 (s, 3H).

$^{13}\text{C NMR}$  (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  151.51, 149.99, 143.18, 127.56, 127.20, 126.72, 121.83, 120.37, 118.99, 82.89, 44.18, 43.29, 40.57, 37.76, 37.66, 32.50, 32.27, 31.70, 31.68, 26.40, 26.20, 21.70, 21.24.

MS (EI)  $M^+ = 348$ , Calc. = 348.52.

Anal. Calc. for  $\text{C}_{25}\text{H}_{32}\text{O}$ : C, 86.15; H, 9.25. Found: C, 86.19; H, 9.15%.

### 3.5. Preparation of (1*R*,3*R*,6*R*,8*R*)-1,2,3,4,5,6,7-Octahydro-2,2,7,7-tetramethyl-1,3:6,8-dimethano-1*H*-fluorene (**4**)

A solution of the alcohol **2** (2.70 g, 9.91 mmol) in THF (250 mL) was treated with concentrated sulfuric acid (0.03 mL, 0.56 mmol) and the resulting mixture was stirred at room temperature for 1 h, after which the reaction mixture was quenched with aqueous 1 N sodium hydroxide solution. The resulting mixture was extracted with *n*-hexane. Combined organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The remained residue was purified by column chromatography on neutral alumina (eluted with *n*-hexane) to give the cyclopentadienes **4** as a yellow solid (1.73 g, 69%), which was an inseparable mixture of diastereomers (ratio = *ca.* -1:1.3).

$^1\text{H NMR}$  (300 MHz,  $\text{C}_6\text{D}_6$ ) (a mixture of diastereomers):  $\delta$  5.74 (s, 1H), 3.49 (m, 2H), 2.78–1.85 (m, 22H), 1.42–1.08 (m, 16H), 0.93 (s, 6H), 0.82 (s, 3H), 0.64 (m, 2H).

$^{13}\text{C NMR}$  (75.5 MHz,  $\text{C}_6\text{D}_6$ ) (a mixture of diastereomers):  $\delta$  151.99, 142.00, 137.42, 136.92, 129.32, 125.86, 123.31, 121.44, 62.38, 56.52, 44.35, 44.01, 43.93, 43.37, 43.06, 42.71, 40.73, 40.52, 37.10, 32.48, 32.31, 31.07, 29.13, 28.82, 27.12, 27.00, 26.79, 26.66, 26.60, 21.91, 21.82, 19.94.

MS (EI)  $M^+ = 254$ , Calc. = 254.41.

Anal. Calc. for  $\text{C}_{19}\text{H}_{26}$ : C, 89.70; H, 10.30. Found: C, 89.71; H, 10.18%.

### 3.6. Preparation of (1*R*,3*R*,6*R*,8*R*)-1,2,3,4,5,6,7,8-Octahydro-9-phenyl-2,2,7,7-tetramethyl-1,3:6,8-dimethanofluorene (**5**)

A solution of the 3° alcohol **3** (1.54 g, 4.42 mmol) in dry diethyl ether (90 mL) was treated with boron trifluoride diethyl etherate (1.09 mL, 8.84 mmol) at 0 °C. The reaction mixture was stirred for 5 h at this temperature. After 5 h, the reaction mixture was quenched with aqueous 1 N sodium hydroxide solution and the mixture was washed

with water. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on neutral alumina (eluted with *n*-hexane) to give **5** as a faint yellow solid (0.87 g, 60%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32–7.12 (m, 5H), 3.97 (s, 1H), 3.07 (t,  $J = 5.4$  Hz, 1H), 2.73–2.51 (m, 6H), 2.18–1.87 (m, 4H), 1.42 (s, 3H), 1.27 (s, 3H), 1.11 (s, 3H), 0.87 (s, 3H), 0.54 (d,  $J = 9.0$  Hz, 1H).

$^{13}\text{C NMR}$  (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.91, 141.29, 138.24, 137.12, 137.02, 128.35, 127.21, 125.13, 56.70, 43.63, 42.62, 42.56, 40.63, 40.61, 40.09, 32.23, 28.92, 27.09, 26.92, 26.71, 26.32, 22.07, 20.16.

MS (EI)  $M^+ = 330$ , Calc. = 330.51.

Anal. Calc. for  $\text{C}_{25}\text{H}_{30}$ : C, 90.85; H, 9.15. Found: C, 90.85; H, 9.33%.

### 3.7. Preparation of (1*R*,3*R*,6*R*,8*R*)-1,2,3,4,5,6,7-Octahydro-2,2,7,7-tetramethyl-1,3:6,8-dimethano-1*H*-fluorenyl dicarbonyl ruthenium(II) chloride (**10**)

A suspension of  $\text{Ru}_3(\text{CO})_{12}$  (0.30 g, 0.47 mmol) and the cyclopentadiene **4** (0.40 g, 1.57 mmol) in *n*-decane (4 mL) was heated to 160 °C for 3 h. (After *ca.* 30 min, the reaction mixture was turned to dark red.) The reaction mixture was cooled to room temperature and concentrated *in vacuo*, after which ethanol (1 mL), chloroform (3 mL), 2 N aqueous HCl (3 mL) and concentrated HCl (0.1 mL) was added. Subsequently,  $\text{O}_2$  was bubbled to the reaction mixture for 4 h and the reaction mixture was extracted with chloroform. The combined organic phase was concentrated *in vacuo* after drying over  $\text{Na}_2\text{SO}_4$ . The remained residue was purified by column chromatography (eluted with 10% ethyl acetate in hexane) to give the half-sandwich complex **10** as a yellow crystalline solid (0.21 g, 33%). X-ray quality crystals were obtained by recrystallization with *n*-hexane.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.12 (s, 1H), 2.85–2.21 (m, 10H), 1.85 (d,  $J = 10.0$  Hz 1H), 1.42 (s, 3H), 1.37 (s, 3H), 1.25 (s, 3H), 1.12 (d,  $J = 9.5$  Hz, 1H), 0.76 (s, 3H).

$^{13}\text{C NMR}$  (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  198.17, 124.73, 119.76, 103.77, 98.96, 62.54, 41.17, 40.94, 40.91, 40.78, 40.75, 40.51, 36.95, 36.79, 27.56, 26.63, 24.94, 24.27, 22.95, 21.88.

ESI-TOF-MS (relative abundance):  $m/z = 411.0906$  (100)  $[\text{M}-\text{Cl}]^+$ , Calc. for  $[\text{M}-\text{Cl}]^+$ : 411.0898.

IR (KBr): 2028, 1967  $\text{cm}^{-1}$ .

Anal. Calc. for  $\text{C}_{21}\text{H}_{25}\text{ClO}_2\text{Ru}$ : C, 56.56; H, 5.65. Found: C, 56.51; H, 5.52%.

### 3.8. Preparation of (1*R*,3*R*,6*R*,8*R*)-1,2,3,4,5,6,7,8-Octahydro-9-phenyl-2,2,7,7-tetramethyl-1,3:6,8-dimethanofluorenyl dicarbonyl ruthenium(II) chloride (**11**)

The phenylated complex **11** was prepared by the same method as the preparation of the non-substituted complex **10** except for the use of **5** and the reaction time of the first step (12 h). The compound **11** was obtained in a yield of 35% as yellow crystalline solid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.31 (m, 3H), 7.14–7.10 (m, 2H), 2.87–2.26 (m, 10H), 1.93 (d,  $J = 10.0$  Hz, 1H), 1.40 (s, 3H), 1.36 (s, 3H), 1.30 (s, 3H), 1.18 (d,  $J = 10.0$  Hz, 1H), 0.84 (s, 3H).

$^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  198.39, 198.34, 130.71, 130.55, 128.72, 128.22, 124.31, 119.54, 101.87, 97.34, 86.75, 40.93, 40.91, 40.87, 40.38, 39.82, 39.57, 36.87, 36.69, 27.59, 26.61, 24.87, 24.14, 23.09, 22.00.

ESI-TOF-MS (relative abundance):  $m/z = 487.1211$  (100)  $[\text{M}-\text{Cl}]^+$ , Calc. for  $[\text{M}-\text{Cl}]^+$ : 487.1220.

IR (KBr): 2022, 1971  $\text{cm}^{-1}$ .

Anal. Calc. for  $\text{C}_{27}\text{H}_{29}\text{ClO}_2\text{Ru}$ : C, 62.12; H, 5.60. Found: C, 62.23; H, 5.69%.

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## Appendix A. Supplementary material

CCDC 652152 and 652153 contain the supplementary crystallographic data for **10** and **11**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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