

cis- β -Ru(II)heteroatom-stabilized-carbene complexes supported by tetradentate Schiff-base salen ligand

Daqing Chen^{a,*}, Xiangguo Guan^b, Qingyun Wan^b, Kam-Hung Low^b, Jie-Sheng Huang^{b,*}

^aSchool of Environment and Ecology, Jiangsu Open University, Nanjing 210000, P. R. China.

^bDepartment of Chemistry, The University of Hong Kong, Hong Kong SAR, P. R. China.

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ABSTRACT

A panel of stable ruthenium carbene complexes bearing a tetradentate salen ligand, with their carbene-C atom adjacent to heteroatom, were synthesized from *cis*- β -Ru(II)-bis(CO) complex by reacting with the corresponding carbene precursors. These carbene complexes, which were fully characterized by elemental analysis, NMR, IR spectroscopy and X-ray-crystal structure determination, all adopt a *cis*- β configuration; the heteroatom (N or O) adjacent to the carbene C atom contributes to the high stability of these complexes both in solution and in solid state. DFT calculations were also performed to gain insight into the Ru-C_{carbene} bonds.

1. Introduction

During the last several decades, tetradentate N₂O₂Schiff-base ligands salens have been widely used to form complexes with transition metal ions for various applications [1-7]. Ruthenium complexes supported by salen ligands have received much attention [8-13], leading to the report of a considerable number of Ru-salen complexes, which are mainly octahedral species adopting *trans* or less frequently *cis*- α or *cis*- β configuration (Fig. 1). The N₂O₂ donor atoms of the salen ligand and the Ru ion in the *trans* complexes are approximately coplanar, while at least one of the two O donor atoms takes the axial coordination site in the *cis*- α or *cis*- β complexes.

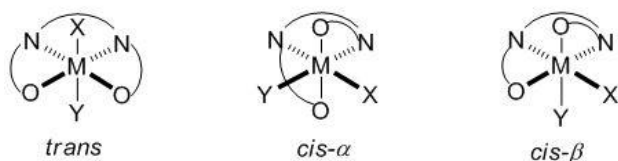


Fig. 1. Three configurations of metal-salen complexes.

Ruthenium-salen complexes with *trans* configurations have been playing a dominant role and widely used as powerful catalysts for many reactions. Interestingly, some *cis*- β -Ru-salen complexes have been reported to show distinct reactivity and better catalytic performance than their *trans* analogues [14-16]. Since the two coordination sites (X and Y in Fig. 1) in *cis*- β -metal-salen complexes are different in steric and electronic nature, this offers great advantages for construction of asymmetric catalysts.

In 2001, Scott and coworkers developed a *cis*- β -bis(acetonitrile) Ru-salen complex for *trans*-selective intermolecular cyclopropanation [17]; exceptionally high stereoselectivity (ee up to 98%, dr up to 99:1) is achieved using ethyl diazoacetate as the carbene source. In 2009, Che and coworkers synthesized a *cis*- β -bis(carbonyl)ruthenium complex with Jacobsen's-salen ligand; this complex can catalyze intramolecular cyclopropanation of *trans*-allylic diazoacetates to give highly enantiopure lactones [15]. Very recently Che and coworkers reported the synthesis of *cis*- β -Ru(II)-complexes supported by sterically encumbered salen ligands and their application in enantioselective carbene Si-H insertion using N₂C(Ar)CO₂ as the carbene source under light irradiation with product yields up to 96% and ee up to 84% [18]. These Ru-catalyzed reactions are proposed to proceed via *cis*- β -Ru-salen carbene intermediates, which are too reactive to be isolated.

In the literature, transition-metal carbene complexes are widely believed to be the active intermediates in a variety of carbene insertions reactions [19-22]. Many of the well characterized transition-metal carbene complexes are supported by macrocyclic N-donor ligands such as porphyrins and macrocyclic tertiary amines [23]; *cis*- β -Ru-carbene complexes bearing salen ligands remain underdeveloped. In Che's recent work, two *cis*- β -[Ru^{II}(salen)(CO)(CAR₂)] complexes, which are stabilized by the α -aryl groups of CAR₂ carbene ligands, were isolated [18]. Herein we report the isolation of [Ru^{II}(salen)(CO)(carbene)] complexes that are stabilized by heteroatom(s) adjacent to the carbene C atom, which contribute unique examples of ruthenium heteroatom-stabilized carbene complexes supported by salens with *cis* configuration.

2. Results and discussion

Treatment of Ru₃(CO)₁₂ with a binaphthyl salen ligand gave *cis*- β -[Ru^{II}(salen)(CO)₂] complex **1**, similar to the reported method for preparation of other *cis*- β -Ru(II)-bis(CO) complexes [15, 18]. Complex **1** is stable in solid form and can be stored for weeks in solid state; however, detectable changes

* Corresponding author.

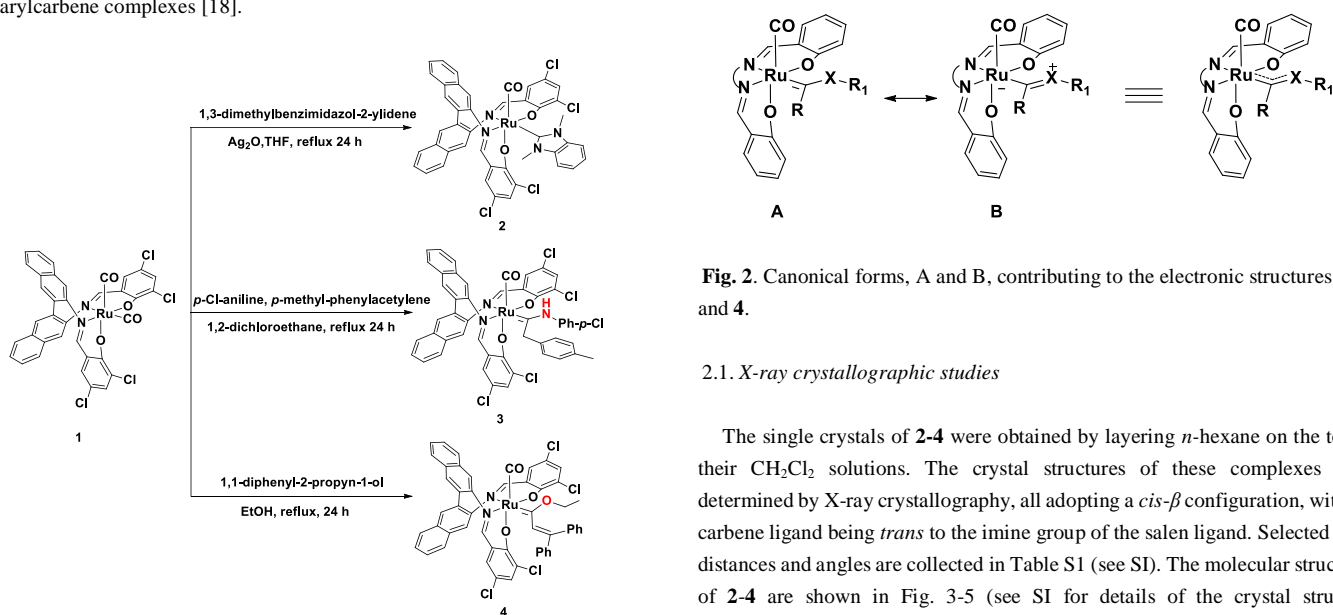
E-mail address: pinkrish@126.com (D. Chen)

E-mail address: jshuang@hku.hk (J.-S. Huang)

were observed by ^1H NMR analysis of a CDCl_3 solution of **1** within a week, with the yellow color gradually turned deep green possibly due to the slow oxidation of Ru(II) to Ru(III) [24-25].

For *cis*- β -[Ru^{II}(salen)(CO)₂] complexes, the Ru-CO bond *trans* to the imine group (weakly π -acidic, reducing Ru \rightarrow CO π -back bonding) is weaker than that *trans* to the O_{phenolate} atom (a π -donor enhancing Ru \rightarrow CO π -back bonding), and thus the CO ligand *trans* to the N_{imine} atom would more readily undergo ligand substitution reaction [18]. Accordingly, the two intense $\nu(\text{CO})$ bands at ~ 2059 and ~ 1993 cm^{-1} in the IR spectra of **1** can be assigned to the CO ligands *trans* to the imine and phenolate groups, respectively.

The previous method for preparing *cis*- β -[Ru^{II}(salen)(CO)(CAR₂)] [18] from *cis*- β -[Ru^{II}(salen)(CO)₂] relies on removal of the CO ligand *trans* to the imine group by photolytic decarbonylation, i.e. under irradiation with an incandescent lamp (300 W), to generate a *cis*- β -[Ru^{II}(salen)(CO)(solvent)] intermediate, which reacted with diazo compounds N_2CAR_2 to give the Ru-diarylcabene complexes [18].



Scheme 1. Synthesis of **2-4**.

In this work, complex **1** was transformed to *cis*- β -[Ru^{II}(salen)(CO)(carbene)] complexes **2-4** by different methods (Scheme 1), which did not need the photolytic decarbonylation step. The *cis*- β -Ru(II)-N-heterocyclic carbene (NHC) complex, *cis*- β -[Ru^{II}(salen)(CO)(NHC)] (**2**), was prepared by directly treating **1** with the corresponding NHC precursor. Complex **3** was obtained by reacting **1** with *p*-chloro-aniline and *p*-methyl-phenylacetylene, which might be conceived as an addition of aniline to a transient Ru=C=C=CHPh allenylidene species. Analogously, treatment of **1** with 1,1-diphenyl-2-propyn-1-ol in ethanol gave **4** through addition of ethanol to a transient Ru=C=C=CPh₂ allenylidene species [26-27].

All the carbene complexes **2-4** have been characterized by NMR spectroscopy, elemental analysis and X-ray crystal structure determination. These complexes exhibited distinctive downfield ^{13}C NMR signals for the C_{carbene} atoms at $\delta = 205.00$, 203.14 and 201.79 ppm for **2**, **3** and **4**, respectively. Unlike **1** (which is not quite stable in solution), complexes **2-4** all showed high stability both in solid form and in solutions. The CDCl_3 solutions of these carbene complexes can be stored at room temperature for weeks and their ^1H NMR spectra showed no noticeable changes. This enhancement in stability is presumably ascribed to the powerful σ -donating ability of these carbene ligands. The weak π -acid imine *trans* to the C_{carbene} atom and the strong π -acid CO ligand *cis* to the C_{carbene} atom both compete for π -back-bonding from the

Ru(II) ion, and the Ru-CO (*trans* to phenolate) π -back bonding in **2-4** is stronger than that in **1**, which resulted in a more robust Ru-CO bond and a weaker C-O bond of the coordinated CO ligand. This is in agreement with the FT-IR studies which revealed that the CO (*trans* to phenolate) stretching frequency decreased from 1993 cm^{-1} in **1** to 1938, 1950 and 1963 cm^{-1} in **2**, **3** and **4**, respectively. And particularly for the Fischer-type carbene complexes **3** and **4**, the carbenic carbon atoms are also stabilized by the hetero N and O atoms (labeled in red, Scheme 1). As π donors, the hetero N and O atoms would reduce the electrophilicity of the carbenic carbon. Thus, two canonical forms contribute to the electronic structure of **3** and **4** as illustrated in Fig. 2. Canonical form B often has a considerable contribution to the electronic structure as manifested by the relatively long Ru-C_{carbene} bond distances (2.017 and 1.977 Å for **3** and **4**, respectively) and short C_{carbene}-X (X= N or O) bond distances (1.313 and 1.304 Å for **3** and **4**, respectively) revealed by the X-ray crystallographic studies.

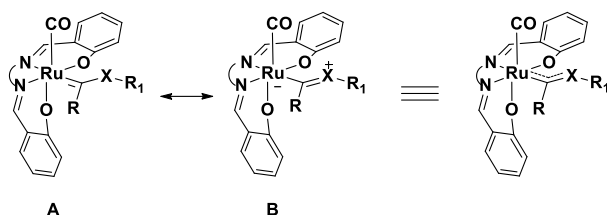


Fig. 2. Canonical forms, A and B, contributing to the electronic structures of **3** and **4**.

2.1. X-ray crystallographic studies

The single crystals of **2-4** were obtained by layering *n*-hexane on the top of their CH_2Cl_2 solutions. The crystal structures of these complexes were determined by X-ray crystallography, all adopting a *cis*- β configuration, with the carbene ligand being *trans* to the imine group of the salen ligand. Selected bond distances and angles are collected in Table S1 (see SI). The molecular structures of **2-4** are shown in Fig. 3-5 (see SI for details of the crystal structure determination). The bond angles around the carbene C atoms all sum up to 360°, in agreement with sp^2 hybridization of these carbene C atoms in **2-4**. There are two independent molecules of **2** in each unit cell of its crystal structure and the average Ru-C_{NHC} distance is 2.069 Å, which is consistent with a normal Ru-C_{NHC} bond. The Ru-C_{carbene} bond distances for **3** and **4** are 2.017 and 1.917 Å, respectively, comparable to those of Ru=C(OR)(CHCPh₂) carbene complexes with arene/phosphine auxiliary ligands [26, 28-30].

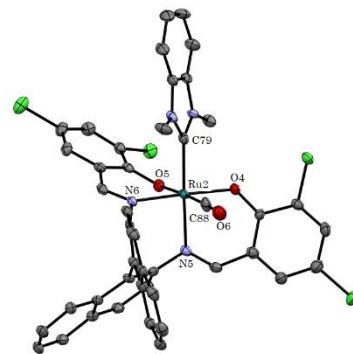


Fig. 3. Molecular structure of **2** (one of the two independent molecules in the crystallographic unit; H atoms and solvent molecules are omitted).

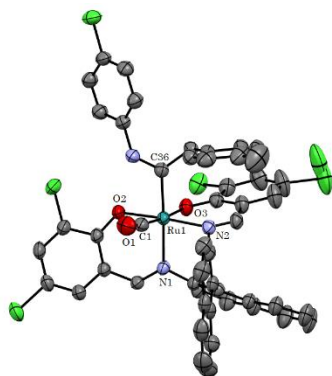


Fig. 4. Molecular structure of **3** (H atoms and solvent molecules are omitted).

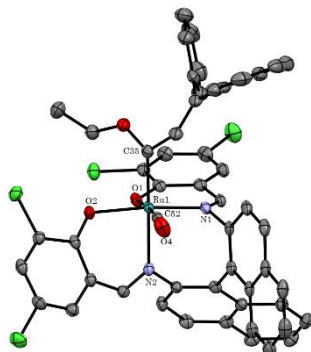


Fig. 5. Molecular structure of **4** (H atoms and solvent molecules are omitted).

2.2 Photophysical properties

UV-visible absorption spectra of **2-4** in CH_2Cl_2 were measured at room temperature (Fig. 6), which show absorption bands at ~ 380 nm, together with intense absorption at < 300 nm, both of which are ascribed mainly to intraligand charge transfer transitions of the salen ligand. The absorption bands at ~ 460 nm are likely due to MLCT transition. There is no significant shift of these absorption bands among **2-4** with **2** displaying the longest MLCT absorption wavelength ($\lambda_{\text{max}} = 463$ nm).

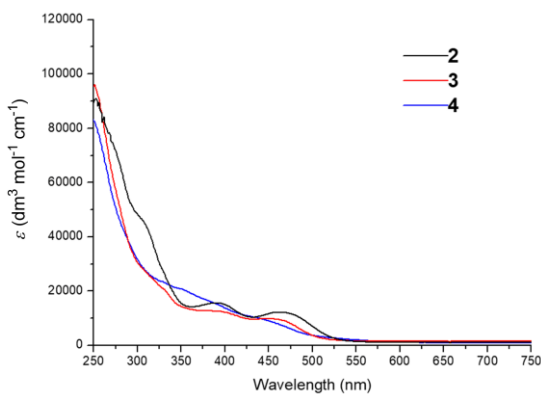


Fig. 6. UV/Vis absorption spectra of **2-4** in CH_2Cl_2 at room temperature.

2.3 Electrochemistry

The redox behaviour of **1-4** in CH_2Cl_2 have been examined by cyclic voltammetry (see Fig. S5-S8 in SI), using $[\text{nBu}_4\text{N}]\text{PF}_6$ as supporting electrolyte. Complexes **1-3** each showed a reversible/quasi-reversible oxidation wave, with $E_{1/2}$ of 1.07, 0.60, and 0.72 V vs Ag/AgCl, respectively; the cathodically shifted $E_{1/2}$ of **2** and **3**, relative to that of **1**, is in accord with replacement of a strong π -

acidic CO ligand (in **1**) with a carbene ligand. Complex **4** displayed an irreversible oxidation wave, with a higher $E_{\text{p,a}}$ (0.82 V vs Ag/AgCl) than those of **2** and **3** (0.64 and 0.75 V vs Ag/AgCl, respectively). This oxidation process is assignable to Ru(II)/Ru(III) oxidation. Among these complexes, **2** displays the lowest oxidation potential, consistent with the electron-donating strength of its NHC ligand.

2.4 Computational studies

The geometries of Ru-salen-carbene complexes **2-4** were optimized at M06L/6-31G*(SDD) [31] level through Gaussian09 program [32]. The calculated key geometrical parameters are in good agreement with the data from X-ray crystallography (see Table S1 in SI).

The bonding interactions between the Ru-salen-CO moiety and the carbene moiety and the bonding interactions between Ru-salen-carbene moiety and the CO moiety for **2-4** based on their DFT-optimized structures have been analyzed by means of the energy decomposition analysis [33-35] (EDA) via ADF2012.01 program [36-38]. The instantaneous interaction energy (ΔE_{int}) between the two fragments can be divided into three main components: $\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$ (ΔE_{Pauli} : repulsive four-electron interactions between occupied orbitals, ΔE_{elstat} : electrostatic interaction energy between unperturbed charge distributions of the prepared fragments, ΔE_{orb} : the stabilizing orbital interaction term). The ΔE_{Pauli} and ΔE_{elstat} can be combined into a single term: $\Delta E_{\text{steric}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}}$.

Table 1

Energy decomposition analysis of Ru(salen)(CO)-carbene at BP86/TZ2P (kcal/mol). Fragment 1 = Ru(salen)(CO), fragment 2 = carbene (**2-4**).

	2	3	4
ΔE_{int}	-60.79	-81.6	-72.7
ΔE_{orb}	-84.14	-110.24	-111.83
ΔE_{steric}	23.35	28.64	39.13
ΔE_{elstat}	-170.63	-199.61	-204.70
ΔE_{Pauli}	193.98	228.25	243.83

The results in Table 1 show that, for **2**, both the ΔE_{int} and ΔE_{orb} are the weakest among these Ru-carbene complexes. This is in line with the fact that Ru-NHC has the longest Ru- $\text{C}_{\text{carbene}}$ distance of 2.057 Å (see Table S1 in SI). The ΔE_{orb} in **3** (-110.24 kcal/mol) is slightly weaker than that in **4** (-111.83 kcal/mol). However, as for the overall bonding interaction, the ΔE_{int} in **3** (-81.6 kcal/mol) is stronger than that in **4** (-72.7 kcal/mol) due to the smaller steric interaction in **3** (28.64 kcal/mol) than that in **4** (39.13 kcal/mol).

Table 2

Energy decomposition analysis of Ru(salen)(carbene)-CO at BP86/TZ2P (kcal/mol). Fragment 1 = Ru(salen)(carbene), fragment 2 = CO (**2-4**).

	2	3	4
ΔE_{int}	-64.45	-58.77	-61.50
ΔE_{orb}	-133.54	-126.25	-128.01
ΔE_{steric}	69.10	67.48	66.51
ΔE_{elstat}	-149.77	-146.28	-145.29
ΔE_{Pauli}	218.86	213.76	211.80

The results from Table 2 show that ΔE_{int} (Ru-CO) of **3** is the weakest and ΔE_{int} (Ru-CO) of **2** is the strongest. As shown in Tables 1 and 2, the trend of ΔE_{int} (Ru-CO) is reverse to the trend of ΔE_{int} (Ru-carbene), which means that stronger bonding interaction between Ru and carbene leads to weaker bonding interaction between Ru and CO.

3. Conclusion

cis- β -Ruthenium heteroatom-stabilized carbene complexes **2-4** bearing a tetradentate salen ligand have been synthesized by reacting *cis*- β -Ru(II)-bis(CO) complex **1** with the corresponding carbene precursors, which represent a new type of isolated *cis*- β -Ru-salen carbene complexes. The transformation of Ru-bis(CO) complex **1** to Ru-(CO)(carbene) complexes **2-4** indicates that the CO ligand (of **1**) *trans* to the salen imine group can be substituted by various heteroatom-stabilized carbene ligands, without the need of photolytic removal of this CO ligand by irradiation with an incandescent lamp, while the CO ligand *trans* to the salen phenolate group remains intact. Spectroscopic and computational studies reveal that the π -backbonding between the Ru center and the remaining CO ligand is enhanced with decreasing π -acceptor ability of the carbene ligand in the *cis* position, which follows the order **2** < **4** < **3**; with **2** having the weakest bonding interaction between Ru and carbene, which leads to the strongest bonding interaction between Ru and CO. This new class of *cis*- β -[Ru^{II}(salen)(CO)(carbene)] complexes, like *cis*- β -[Ru^{II}(salen)(CO)₂] [15, 18] and *cis*- β -[Ru^{II}(salen)(CO)(CAR₂)] [18] analogues, may serve as potential catalysts for organic transformations such as intramolecular carbene transfer reactions. The catalytic applications of **2-4** and activation of the remaining CO group in this type of complexes to generate a chiral cage and active reaction site for catalysis are under investigation.

4. Experimental Section

Starting materials were purchased from commercial sources and were used as received and the reactions were conducted under an inert atmosphere, unless otherwise stated. THF was distilled from sodium-benzophenone. EtOH was distilled from sodium. The solvents used for photophysical measurements were of HPLC grade. Elemental analyses were performed by the Institute of Chemistry at the Chinese Academy of Sciences, Beijing, P. R. China. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat95 mass spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on DPX300 and Avance500 Bruker FT-NMR spectrometers. UV-vis absorption spectra were recorded on a PerkinElmer Lambda19 UV/vis spectrophotometer. Cyclic voltammetric measurements were performed with a Princeton Applied Research electrochemical analyzer (potentiostat/galvanostat Model 273A). [Bu₄N]PF₆ (0.1 M) in CH₂Cl₂ was used as a supporting electrolyte for the electrochemical measurements at room temperature. All solutions used in electrochemical measurements were deaerated with argon gas. Ag/AgCl (0.1 M in MeCN), a glassy-carbon electrode, and a platinum wire were used as reference electrode, working electrode, and counter electrode, respectively.

4.1 Complex 1

To a degassed 25 mL round-bottomed flask, Ru₃(CO)₁₂ (364.79 mg, 0.57 mmol) and the H₂salen ligand (359.12 mg, 0.57 mmol) were added under argon atmosphere, followed by addition of 1,2,4-trichlorobenzene (15 mL). The mixture was stirred in the absence of light at 190-195 °C for 6 h and then cooled to room temperature. After flash chromatography on silica gel column with *n*-hexane/EtOAc (5:1 v/v) as eluent, the product was recrystallized from a CH₂Cl₂/MeOH solution and dried. Yield: 31%; ¹H NMR (CDCl₃, 300 MHz) δ 8.14 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.88-7.84 (m, 2H), 7.57-7.44 (m, 3H), 7.39-7.30 (m, 4H), 7.27-7.25 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 2.6 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 2.6 Hz, 1H); IR 2059, 1993 cm⁻¹ (ν (CO)); FAB-MS *m/z* 785 [M]⁺. Anal Calcd for C₃₆H₁₈Cl₄N₂O₄Ru: C, 55.05; H, 2.31; N, 3.57. Found: C, 55.10; H, 2.37; N, 3.51.

4.2 Complex 2

Excess 1,3-dimethyl-1H-benzimidazolium iodide (0.5 mmol) and silver(I) oxide (0.3 mmol) were added to **1** (0.1 mmol) in THF (10 mL). After refluxing for 24 h, the solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on a silica gel column with *n*-hexane/EtOAc(1:20~1:5 v/v) as eluent; the product was recrystallized from a CH₂Cl₂/*n*-hexane solution and dried. Yield: 83%; ¹H NMR(CDCl₃, 300 MHz) δ 8.12 (d, *J* = 8.7 Hz, 1H), 8.06 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.87-7.78 (m, 2H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.54-7.49 (m, 1H), 7.42 (s, 1H), 7.41-7.29 (m, 3H), 7.25-7.21 (m, 4H), 7.17-7.12 (m, 3H), 7.07 (d, *J* = 2.7 Hz, 1H), 7.00 (d, *J* = 2.7 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.33 (d, *J* = 2.7 Hz, 1H), 4.31 (s, 6H); ¹³C NMR(CDCl₃, 125MHz) δ 205.00 (Ru=C); IR 1938 cm⁻¹ (ν (CO)); FAB-MS *m/z* 903 [M]⁺. Anal Calcd for C₄₄H₂₈Cl₄N₄O₃Ru: C, 58.49; H, 3.12; N, 6.20. Found: C, 58.60; H, 3.17; N, 6.11.

4.3 Complex 3

Excess *p*-methylphenylacetylene (0.5 mmol) and *p*-chloroaniline (0.3 mmol) were added to **1** (0.1 mmol) in 1,2-dichloroethane (10 mL). After refluxing for 24 h, the solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on a silica gel column with *n*-hexane/ EtOAc as eluent; the product was recrystallized from a CH₂Cl₂/*n*-hexane solution and dried. Yield: 29%; ¹H NMR(CDCl₃, 400 Hz) δ 12.29 (s, 1H), 8.09 (s, 1H), 7.88-7.81 (m, 3H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.45-7.38 (m, 2H), 7.37 (s, 1H), 7.34 (d, *J* = 2.7 Hz, 1H), 7.31-7.27 (m, 3H), 7.25-7.24 (m, 1H), 7.20-7.16 (m, 2H), 7.07-7.05 (m, 4H), 7.02-6.99 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 2H), 6.58 (d, *J* = 2.7 Hz, 1H), 4.09 (s, 2H), 2.35 (s, 3H); ¹³C NMR(CDCl₃, 125MHz) δ 203.14 (Ru=C); IR 1950 cm⁻¹ (ν (CO)); FAB-MS *m/z* 1001 [M]⁺. Anal Calcd for C₄₉H₃₂Cl₃N₃O₂Ru: C, 60.48; H, 3.31; N, 4.32. Found: C, 60.62; H, 3.40; N, 4.21.

4.4 Complex 4

Excess 1,1-diphenyl-2-propyn-1-ol (0.5 mmol) was added to **1** (0.1 mmol) in EtOH (10 mL). After refluxing for 24 h, the solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel column with *n*-hexane/EtOAc as eluent; the product was recrystallized from a CH₂Cl₂/*n*-hexane solution and dried. Yield: 79%; ¹H NMR(CDCl₃, 500Hz) δ 8.08 (s, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 8.1Hz, 1H), 7.83-7.80 (m, 2H), 7.51-7.49 (m, 2H), 7.48-7.11 (m, 17H), 6.99 (d, *J* = 2.7 Hz, 1H), 6.87-6.84 (m, 3H), 6.56 (d, *J* = 2.7 Hz, 1H), 5.35-5.24 (m, 2H), 0.81 (t, *J* = 7.1 Hz, 3H); ¹³C NMR(CDCl₃, 125MHz) δ 201.79 (Ru=C); IR 1963 cm⁻¹ (ν (CO)); FAB-MS *m/z* 993 [M]⁺. Anal Calcd for C₅₁H₃₄Cl₄N₂O₃Ru: C, 63.43; H, 3.55; N, 2.90. Found: C, 63.61; H, 3.50; N, 2.81.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

CCDC 1964684, 1966539 and 922701 contain the supplementary crystallographic data for complexes **2**, **3** and **4**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/xxxxxx>

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