

Diruthenium compounds of heterocycle-containing acetylides

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Dedicated to the memory of Professor Al Cotton, mentor, scholar, and friend.

Abstract

Novel diruthenium compounds containing heterocycle-acetylide are reported here. $\text{Ru}_2(\text{Y-DMBA})_4(\text{C}\equiv\text{C-2-pyrimidine})_2$ were prepared from the reaction between $\text{Ru}_2(\text{Y-DMBA})_4(\text{NO}_3)_2$ and $\text{HC}\equiv\text{C-2-pyrimidine}$ in the presence of Et_2NH , where Y-DMBA is either *N,N'*-dimethylbenzamidinate (DMBA, Y = H) or *N,N'*-dimethyl-(3-methoxy)benzamidinate (Y = 3- CH_3O). $\text{Ru}_2(\text{Y-DMBA})_4(\text{C}\equiv\text{C-4-}N\text{-methylpyridinium})_2$ were obtained through the methylation of known compounds $\text{Ru}_2(\text{Y-DMBA})_4(\text{C}\equiv\text{C-4-pyridine})_2$. Both the structural and voltammetric data are consistent with the heterocycles being moderate electron acceptors.

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1. Introduction

The chemistry of metal-acetylides has been a prosperous one [1]. Early studies focused on the synthesis and properties of simple mononuclear species [2]. Because of both the structural rigidity and extended π -conjugation of acetylenic bonds, attention was shifted to the preparation of conjugated polymers based on metal-acetylide monomers in the 80s and early 90s, and work from the laboratories of Hagihara [3] and Lewis [4] were most noteworthy. It was soon realized that the degree of conjugation along the metal-acetylide backbone is very limited due to the closed shell nature of M^{I} (M = Cu, Ag and Au) and stable d^8 configuration of M^{II} (M = Pd and Pt) [5]. Hence, much of the efforts since the mid 90s have been focusing on acetylide compounds of middle transition metals [6], and excellent electronic couplings were demonstrated with M as Fe [7], Ru [8], Mn [9] and Re [10]. In several instances, metal phenylacetylide compounds were interrogated with various nano-junction techniques and interesting current–voltage characteristics were observed [11].

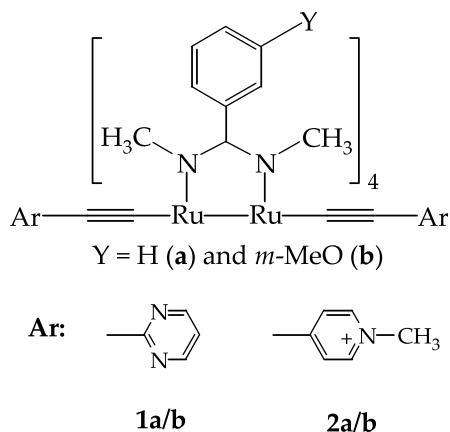
Compared with the afore-mentioned mononuclear acetylide species, diruthenium acetylide compounds are unique in both the molecular and electronic structures, especially the rich and complex redox activities [12,13]. We previously reported a series of symmetrical $\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{CAr})_2$ (DMBA: *N,N'*-dimethylbenzamidinate) compounds where Ar is phenyl bearing electron donor or acceptor substituent, and the effect of the donor/acceptor substitution on the electronic nature of these diruthenium species [14]. More recently, unsymmetric $(\text{ArC}\equiv\text{C})\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{CAr}')$ ($\text{Ar} \neq \text{Ar}'$) type compounds were synthesized under the optimized conditions and the electronic asymmetry in compounds of D- Ru_2 -A arrangement was elaborated [15]. Described in this contribution are the synthesis and characterization of symmetric $\text{Ru}_2(\text{Y-DMBA})_4(\text{C}\equiv\text{CAr})_2$ (Y = H, **1**; *m*-MeO, **2**) with Ar as heterocyclic rings (see Scheme 1).

2. Results and discussion

2.1. Synthesis

The weak base assisted protocol has been proven as an efficient method for the preparation of $\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{CAr})_2$ type compounds [14–16]. As shown in

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Scheme 1. Structures of compounds **1** and **2**.

Scheme 2, the reaction between $\text{Ru}_2(\text{Y-DMBA})_4(\text{NO}_3)_2$ (Y = H(**a**) and Y = *m*MeO (**b**)) and $\text{HC}\equiv\text{C}-2\text{-N}_2\text{C}_4\text{H}_3$ (2–5 equiv) [17] in the presence of Et_2NH afforded compounds **1a/b** in satisfactory yield. Treating $\text{Ru}_2(\text{Y-DMBA})_4(\text{C}\equiv\text{C}-4\text{-C}_5\text{H}_4\text{N})_2$ [15] with iodomethane in THF resulted in the corresponding *N*-methylpyridinium derivatives **2a/b** in excellent yield. Isolated as the iodide salt, compounds **2a/b** are insoluble in THF but very soluble in acetone. All four compounds are red, diamagnetic materials, and were unambiguously identified using ^1H NMR, MS (FAB or ESI) and combustion analysis techniques. Metal- $\sigma\text{-C}\equiv\text{C}$ -*N*-alkylpyridinium compounds are known in literature, and they were generally prepared through the alkylation of corresponding metal- $\sigma\text{-C}\equiv\text{C}$ -pyridine species [18]. Metal complexes containing σ -(pyrimidine)ethynyl ligand, however, remains unknown to our knowledge. Synthetic procedures reported herein should be of interest to the metal-acetylide community.

2.2. Structural studies

Molecular structures of compounds **1a** and **2b** were determined through X-ray single crystal diffraction study, and their structural plots are presented in Figs. 1 and 2. The selected bond lengths and angles of both structures are given in Table 1. Compound **1a** crystallizes in the monoclinic space group $P2_1/n$, and the asymmetric unit contains one half of independent molecule **1a**, which is related to the other half via an inversion center. Compound **2b** crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit contains one independent molecule. Overall topological features of compounds **1a** and **2b** are similar to those of previously characterized $\text{Ru}_2(\text{DMBA})_4(\text{C}_2\text{R})_2$,

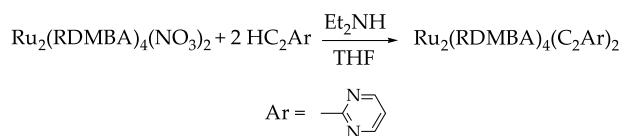
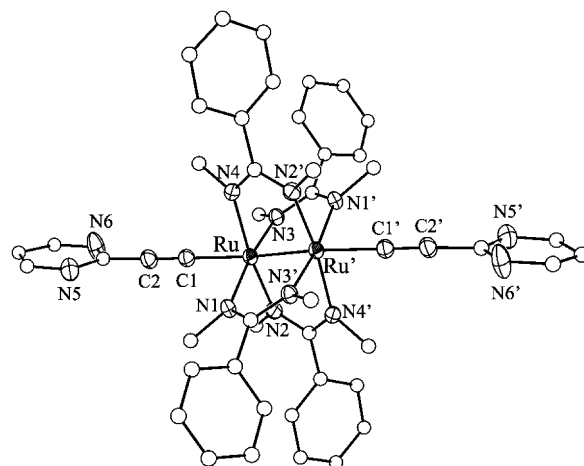
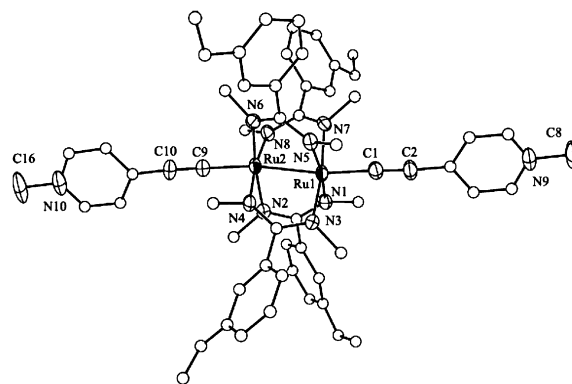
Scheme 2. Preparation of compounds **1**.Fig. 1. Structural plot of molecule **1a** at 30% probability level. All hydrogen atoms are omitted for clarity.Fig. 2. Structural plot of molecule **2b** at 30% probability level. All hydrogen atoms and counter anion (I^-) are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for compounds **1a**, and **2b**

1a		2b	
Ru–Ru'	2.4519(6)	Ru1–Ru2	2.4542(7)
Ru–N1	2.146(3)	Ru1–N1	2.044(5)
Ru–N2	1.993(3)	Ru1–N3	2.001(5)
Ru–N3	1.988(3)	Ru1–N5	2.061(5)
Ru–N4	2.135(3)	Ru1–N7	2.084(5)
		Ru2–N2	2.070(6)
		Ru2–N4	2.069(5)
		Ru2–N6	2.023(5)
		Ru2–N8	2.000(5)
Ru–C1	1.975(4)	Ru1–C1	1.929(7)
		Ru2–C9	1.923(7)
C1–C2	1.206(5)	C1–C2	1.225(9)
		C9–C10	1.228(9)
		C8–N9	1.479(9)
		C16–N10	1.50(1)
C1–Ru–Ru'	157.6(1)	C1–Ru1–Ru2	170.9(2)
		C9–Ru2–Ru1	171.4(2)

including the hallmark structural distortion (large variations among Ru–N bond lengths and bent of Ru–Ru– C_α linkage) that is attributed to a second order Jahn–Teller effect [19]. The Ru–Ru bond lengths in compound **1a**

(2.4519(6) Å) and **2b** (2.4542(7) Å) are almost identical and consistent with the existence of a Ru–Ru single bond. These bond lengths are intermediate between those of Ru₂(*m*MeO–DMBA)₄(C₂Ph)₂ (2.448(1) Å) and Ru₂(DMBA)₄(CCC₆H₄NO₂)₂ (2.459(1) Å) [14]. Since the degree of elongation of Ru–Ru bond is proportional to the electron-withdrawing ability of Ar, both pyrimidine and *N*-methylpyridinium appear to be moderate electron acceptors.

2.3. Electrochemistry

The redox behavior of compounds **1** were studied with cyclic voltammetry technique in THF (Fig. 3), while that of compounds **2** in acetone (Fig. 4) due to the ionic nature of **2**. The electrode potentials of compounds **1**, **2** and Ru₂(DMBA)₄(C₂Ph)₂ [14] are collected in Table 2.

CVs shown in Figs. 3 and 4 all feature two main waves: the one electron oxidation (A) and one electron reduction (B), which are both Ru₂-based processes [12]. While the couple B of compound **1a** is reversible, all other couples are quasi-reversible judging from significant deviations from unity in their $i_{\text{backward}}/i_{\text{forward}}$ ratios. In comparison, Ru₂(Y-DMBA)₄(C≡CAr)₂ with Ar as a substituted phenyl usually display more reversible couples [14]. In addition, compounds **1** display a small wave near 0.20 V (C) on the backward anodic sweep, indicating a partial degradation

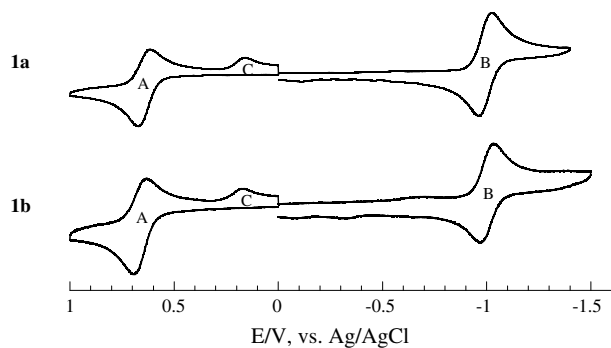


Fig. 3. CVs of compounds **1a** and **1b** recorded in THF at a scan rate of 0.10 V/s.

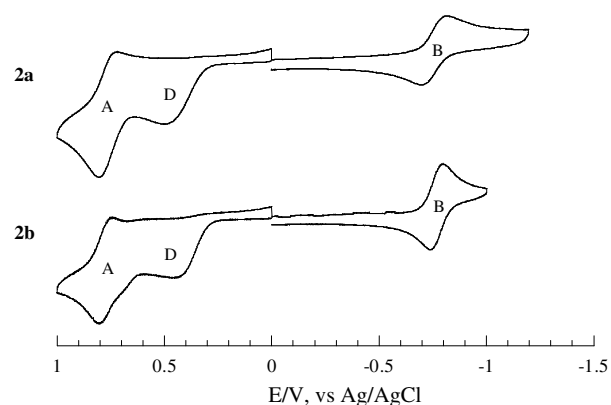


Fig. 4. CVs of compounds **2** recorded in acetone at a scan rate of 0.10 V/s.

Table 2
Electrode potentials (V) for compounds **1** and **2**

Compd	$E_{1/2}$ (A)	$E_{1/2}$ (B)
1a	0.66	-0.95
1b	0.67	-1.00
2a	0.78	-0.76
2b	0.77	-0.77
Ru ₂ (DMBA) ₄ (C ₂ Ph) ₂	0.52	-1.10

of **1** that is absent in typical CVs of Ru₂(Y-DMBA)₄(C≡CAr)₂ [14]. Compounds **2** exhibit a more pronounced wave around 0.40 V (D) in the forward anodic sweep, which has not been observed in any other compound of the Ru₂(Y-DMBA)₄(C≡CR)₂ type and its origin remains unidentified presently.

Prior studies of both the symmetric Ru₂(Y-DMBA)₄(C≡CAr)₂ and asymmetric (Ar'C≡C)Ru₂(DMBA)₄(C≡CAr) (Ar' ≠ Ar) compounds revealed that the electrode potentials of both A and B couples are dependent on the nature of aryl substituent: the potentials shift cathodically with a donor substituent and anodically with an acceptor [14,15]. In compounds **1** and **2**, heterocyclic rings are acceptor groups themselves. Hence, the potentials of both the oxidation and reduction couples in **1a** are anodically shifted by about 0.14 V from those of Ru₂(DMBA)₄(C≡CPh)₂. Prior study of Ru₂(DMBA)₄(C≡C-4-py)₂ revealed an anodic shift of *ca.* 0.18 V [15]. Presence of cationic *N*-methylpyridinium in compound **2** imparts more pronounced effect on the Ru₂ center with the potential shifts ranging 0.25–0.34 V.

2.4. Vis–NIR spectra studies

The Vis–NIR spectra of compounds **1** were recorded in THF, and those of **2** recorded in acetone (Fig. 5). Similar

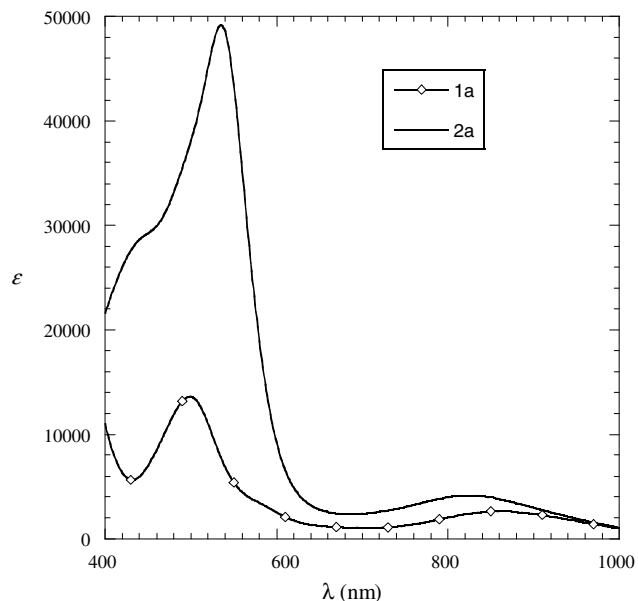


Fig. 5. Vis–NIR spectra of compounds **1a** (in THF) and **2a** (in acetone).

to $\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{C}\text{Ar})_2$ [14], all compounds exhibit two major bands: the first with $\lambda_{\text{max}}(\text{nm})$ around 494 for **1** and 535 for **2**, and the second with λ_{max} around 860 for **1** and 820 for **2**. As analyzed in the early studies [20], the band of lower energy can be assigned to the $\pi^*(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$ transition, where the axial alkyne ligand contributes through the antibonding overlap between $\pi(\text{C}\equiv\text{C})$ and $\pi^*(\text{Ru}_2)$. The band of higher energy is primarily the $\text{L}(\text{N}) \rightarrow \delta^*(\text{Ru}_2)$ transition with a minor component of $\delta(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$. Consistent with the assignment of a CT transition, the spectrum recorded in acetone (**2a**) is far more intense than that recorded in THF (**1a**) near 500 nm.

2.5. Conclusions

Results reported here demonstrated both the feasibility to prepare heteroaryl-ethynyl Ru_2 compounds and the electron acceptor nature of heteroaryls. It is thus possible to prepare the analogues of the recently reported Donor- Ru_2 -Acceptor compounds [15] with a heteroaryl group as the acceptor component, and this aspect is being investigated in our laboratory.

3. Experimental

3.1. General

$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, iodomethane, 4-ethynylpyridine hydrochloride and 2-bromopyrimidine were purchased from Aldrich, diethylamine, and $\text{PhC}\equiv\text{CH}$ from ACROS, trimethylsilylacetylene from GFS, and silica gel from Merck. $\text{Ru}_2(\text{DMBA})_4(\text{NO}_3)_2$ were prepared according to the literature. 2-Ethynylpyrimidine was prepared from the *Sonogashira* reaction between 2-bromopyrimidine and trimethylsilylacetylene followed by desilylation with excess of K_2CO_3 in THF/ CH_3OH (1/1, v/v) [21]. THF was distilled over Na/benzophenone under an N_2 atmosphere prior to use. ^1H NMR spectra were recorded on a Bruker AVANCE300 NMR spectrometer. Mass spectra were recorded on either a VG Trio-2 mass spectrometer (FAB) or a FinniganMAT XL95 mass spectrometer (ESI). Vis-NIR spectra were obtained with a Perkin-Elmer Lambda-900 UV-Vis-NIR spectrophotometer. Cyclic voltammograms were recorded in 0.2 M (*n*-Bu) $_4\text{NPF}_6$ solution on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a Ag/AgCl reference electrode. The concentration of diruthenium species is always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.586 V in THF and at 0.595 V in acetone (*vs.* Ag/AgCl) under experimental conditions.

3.2. Synthesis of $\text{Ru}_2(m\text{-MeODMBA})_4(\text{C}\equiv\text{C-}4\text{-C}_5\text{H}_4\text{N})_2$

A mixture of 0.300 g (0.32 mmol) of $\text{Ru}_2(\text{DMBA})_4(\text{NO}_3)_2$, 0.137 g (0.98 mmol) of 4-ethynylpyridine

hydrochloride, and 0.220 g (1.96 mmol) of potassium *tert*-butoxide in 200 mL THF was stirred under argon at room temperature overnight. The color of the reaction mixture changed from dark green to dark red during the reaction. The reaction mixture was filtered through a plug of silica gel. Upon the solvent removal, the residue was purified by recrystallization from THF and hexanes to yield a reddish solid 0.240 g (75%). Data: ^1H NMR (CDCl_3): 8.30 (d, 4H, aromatic), 7.44–7.38 (m, 12H, aromatic), 6.90 (d, 8H, aromatic), 6.88 (d, 4H, aromatic), 3.24 (s, 24H, MeN-); MS-FAB (*m/e*, based on ^{101}Ru): 997 [M^+H]; Vis-NIR, $\lambda_{\text{max}}(\text{nm}, \epsilon(\text{M}^{-1}\text{cm}^{-1}))$: 839(2,320), 500(9,990); Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{\text{backward}}/i_{\text{forward}}$: **A**, 0.616, 0.056, 0.687; **B**, -0.996, 0.063, 0.950. Anal. Calc. for $\text{C}_{50}\text{H}_{52}\text{N}_{10}\text{Ru}_2 \cdot \text{H}_2\text{O}$: C, 59.27; H, 5.37; N, 13.82. Found: C, 59.75; H, 5.43; N, 13.62%.

3.3. Synthesis of $\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{C-}4\text{-N}_2\text{C}_4\text{H}_3)_2$ (**1a**)

To a suspension of 0.20 g (0.22 mmol) of $\text{Ru}_2(\text{DMBA})_4(\text{NO}_3)_2$ in 70 mL THF were added 0.050 g (0.48 mmol) of 4- $\text{C}_4\text{H}_3\text{N}_2\text{-C}\equiv\text{CH}$ and 20 mL of Et_2NH . The reaction mixture was stirred at room temperature for 2 h. Upon the solvent removal, the residue was purified on a silica column with CH_2Cl_2 /hexanes (1/1, v/v) to afford reddish solid 0.100 g (45%). Data: ^1H NMR (CDCl_3): 8.55 (d, 4H, aromatic), 7.45–7.41 (m, 12H, aromatic), 7.03–7.01 (m, 8H, aromatic), 6.80 (*t*, 2H, aromatic), 3.31 (s, 24H, MeN-); MS-FAB (*m/z*, based on ^{101}Ru): 999 [M^+H]; Vis-NIR, $\lambda_{\text{max}}(\text{nm}, \epsilon(\text{M}^{-1}\text{cm}^{-1}))$: 859(2,630), 499(13,600); Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{\text{backward}}/i_{\text{forward}}$: **A**, 0.661, 0.059, 0.856; **B**, -0.949, 0.065, 0.953. Anal. Calc. for $\text{C}_{48}\text{H}_{50}\text{N}_{12}\text{Ru}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 56.03; H, 4.94; N, 16.17. Found: C, 56.43; H, 5.05; N, 15.83%.

3.4. Synthesis of $\text{Ru}_2(\text{MeODMBA})_4(\text{C}\equiv\text{C-}4\text{-N}_2\text{C}_4\text{H}_3)_2$ (**1b**)

To a suspension of 0.200 g (0.19 mmol) of $\text{Ru}_2(\text{MeODMBA})_4(\text{NO}_3)_2$ in 70 mL THF were added 0.100 g (0.96 mmol) of 4- $\text{C}_4\text{H}_3\text{N}_2\text{-C}\equiv\text{CH}$ and 20 mL of Et_2NH . The reaction mixture was stirred at room temperature for 2 h. Upon the solvent removal, the residue was purified on a silica column with THF/hexanes (1/1, v/v) to afford reddish solid 0.160 g (75%). Data: ^1H NMR (CDCl_3): 8.38 (d, 4H, aromatic), 7.37–7.291 (m, 2H, aromatic), 6.97–6.79 (m, 8H, aromatic), 6.60–6.53 (m, 8H, aromatic), 3.75 (s, 12H, MeO-), 3.44 (s, 24H, MeN-); MS-ESI (*m/z*, based on ^{101}Ru): 1117 [M^+H]; Vis-NIR, $\lambda_{\text{max}}(\text{nm}, \epsilon(\text{M}^{-1}\text{cm}^{-1}))$: 852(2,660), 494(14,900); Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{\text{backward}}/i_{\text{forward}}$: **A**, 0.665, 0.055, 0.667; **B**, -1.002, 0.064, 0.844. Anal. Calc. for $\text{C}_{52}\text{H}_{58}\text{N}_{12}\text{O}_4\text{Ru}_2 \cdot 5\text{THF}$: C, 58.52; H, 6.68; N, 11.37. Found: C, 58.58; H, 6.26; N, 11.24%.

3.5. Synthesis of $[Ru_2(DMBA)_4(C\equiv C-4-C_5H_4N-Me)_2]I_2$ (**2a**)

To a mixture of 0.070 g (0.07 mmol) of $Ru_2(DMBA)_4(C\equiv CC_6H_4-4-C_5H_4N)_2$ in 50 mL THF was added 0.5 mL (0.08 mmol) of CH_3I . The reaction mixture was stirred at room temperature for 6 h. The precipitate was collected through filtration and rinsed with THF. Recrystallization from acetone and hexane gave 0.080 g reddish crystals of **2a** (88% based on Ru). Data: 1H NMR (CD_3COCD_3): 8.75 (d, 4H, aromatic), 7.57 (d, 16H, aromatic), 7.18–7.15 (m, 8H, aromatic), 4.41 (s, 6H, CH_3N^-), 3.38 (s, 24H, CH_3N^-); MS-FAB (m/z , based on ^{101}Ru): 1026 $[M-2I]^+$; Vis-NIR, λ_{max} (nm, $\epsilon(M^{-1}cm^{-1})$): 820(4,120), 535(49,200), 540(sh); Electrochemistry (Acetone), $E_{1/2}/V$, $\Delta E_p/V$, $i_{backward}/i_{forward}$: (in acetone) **A**, 0.784, 0.087, 0.534; **B**, -0.761, 0.117, 0.871. Anal. Calc. for $C_{52}H_{58}I_2N_{10}Ru_2 \cdot 2H_2O$: C, 47.49; H, 4.75; N, 10.65. Found: C, 47.53; H, 4.73; N, 10.66%.

3.6. Synthesis of $[Ru_2(MeODMBA)_4(C\equiv C-4-C_5H_4N-Me)_2]I_2$ (**2b**)

To a mixture of 0.020 g (0.018 mmol) of $Ru_2(MeODMBA)_4(C\equiv CC_6H_4-4-C_5H_4N)_2$ in 20 mL THF was added 0.2 mL (0.032 mmol) of CH_3I . The reaction mixture was stirred at room temperature for 6 h. The precipitate was collected through filtration and rinsed with THF. Recrystallization from acetone and hexane gave 0.018 g reddish crystals of **2b** (87% based on Ru). Data: 1H NMR (CD_3COCD_3): 8.72 (d, 4H, aromatic), 7.61–7.49 (m, 8H, aromatic), 6.61–6.59 (m, 8H, aromatic), 7.14–7.10 (m, 4H, aromatic), 6.61–6.59 (m, 8H, aromatic), 4.39 (s, 6H, CH_3N^-), 3.85 (s, 12H, CH_3O^-), 3.36 (t, 24H, CH_3N^-); MS-FAB (m/z , based on ^{101}Ru): 1147 $[M]^+$; Vis-NIR, λ_{max} (nm, $\epsilon(M^{-1}cm^{-1})$): 819(4,490), 535(54,600); Electrochemistry (Acetone), $E_{1/2}/V$, $\Delta E_p/V$, $i_{backward}/i_{forward}$: (in acetone) **A**, 0.769, 0.062, 0.666; **B**, -0.768, 0.056, 0.786. Anal. Calc. for $C_{56}H_{66}I_2N_{10}O_4Ru_2 \cdot 2H_2O$: C, 46.87; H, 4.92; N, 9.76. Found: C, 46.68; H, 4.77; N, 9.62%.

3.7. Structure determination

Single crystals were obtained by slow evaporation of hexanes-THF solution **1a**, and slow diffusion of hexanes into an acetone solution **2b**. X-ray intensity data were measured at 300 K on a Bruker SMART1000 CCD-based X-ray diffractometer system using Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$). For data collection, thin plates of dimensions $0.20 \times 0.20 \times 0.05 \text{ mm}^3$ (**2b**) was wedged in a 0.20 mm capillary filled with mother liquor, and $0.19 \times 0.13 \times 0.03 \text{ mm}^3$ (**1a**) was cemented onto a quartz fiber with epoxy glue. Data were measured using omega scans of 0.3° per frame such that hemisphere (1271 frames) was collected. The frames were integrated with the Bruker SAINT[®] software package [22] using a narrow-frame integration algorithm,

Table 3
Crystallographic parameters for compounds **1a** and $[2b]I_2 \cdot H_2O$

	1a	$[2b]I_2 \cdot H_2O$
Formula	$C_{48}H_{50}N_{12}Ru_2$	$C_{50}H_{72}I_2N_{10}O_6Ru_2$
F_w	997.14	1473.21
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	11.2352(6)	14.3553(8)
b (Å)	12.2544(7)	15.8454(9)
c (Å)	15.9200(9)	17.485(1)
α (°)		65.630(1)
β (°)	93.692(1)	85.429(1)
γ (°)		64.093(1)
Volume (Å ³)	2187.3(2)	3234.1(3)
Z	2	2
D_{calcd} (g cm ⁻³)	1.514	1.513
μ (mm ⁻¹)	0.740	1.475
Radiation	Mo $K\alpha$	Mo $K\alpha$
T (K)	300	300
R_1, wR_2 ($I > 2\sigma(I)$)	0.041, 0.103	0.056, 0.150

which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS.

Structures were solved and refined using the Bruker SHELXTL[®] (Version 5.1) software package [23] in space groups of $P\bar{1}$ (**2b**) and $P2_1/n$ (**1a**). Positions of all non-hydrogen atoms were revealed by direct method. All non-hydrogen atoms are anisotropic and the hydrogen atoms were put in calculated positions and riding mode. Each structure was refined to convergence by least squares method on F^2 , SHELXL-93, incorporated in SHELXTL.PC V 5.03. Crystallographic data are given in Table 3.

Acknowledgements

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Appendix A. Supplementary material

CCDC 651062, 651063 contain the supplementary crystallographic data for **1a** and **2b**. These data can be obtained free of charge via <http://www.ccdc.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. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.08.001](https://doi.org/10.1016/j.jorganchem.2007.08.001).

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