

Further molecular engineering of diruthenium-(2-anilinopyridinate) alkynyl compounds through ligand design

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

Abstract

A modified *ap* ligand, 2-(3,5-dimethoxyanilino)pyridine (HDiMeO*ap*) and its diruthenium compounds $\text{Ru}_2(\text{DiMeOap})_4\text{Cl}$ (**1**), $\text{Ru}_2(\text{DiMeOap})_4(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)$ (**2**) and $\text{Ru}_2(\text{DiMeOap})_4(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2$ (**3**) were prepared and characterized. New compounds $\text{Ru}_2(\text{MeOap})_4(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_x$ ($x = 1, \mathbf{4}; 2, \mathbf{5}$; MeO*ap* is 2-(3-methoxyanilino)pyridinate) were prepared from the previously reported $\text{Ru}_2(\text{MeOap})_4\text{Cl}$. In addition, two related diruthenium compounds containing ferrocenyl acetylide ligand, $\text{Ru}_2(\text{MeOap})_4(\text{C}\equiv\text{CFc})$ (**6**) and $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CC}\equiv\text{CFc})$ (**7**), were synthesized. Molecular structures of compounds **1**, **2**, **6** and **7** were established using single crystal X-ray diffraction study.

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1. Introduction

The chemistry of diruthenium paddlewheel species containing axial alkynyl ligands began with the report of $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CPh})$ (*ap* = 2-anilinopyridinate, Chart 1) by Chakravarty and Cotton in 1986 [1]. Several families of diruthenium alkynyl compounds have since emerged including those based on $\text{Ru}_2(\text{DARF})_4$ (DARF = diarylformamidinate) [2], $\text{Ru}_2(\text{ap})_4$ and $\text{Ru}_2(\text{F}_x\text{ap})_4$ (F_xap = 2-(fluoroanilino)-pyridinate) [3–5] and $\text{Ru}_2(\text{DMBA})_4$ (DMBA = *N,N'*-dimethylbenzamidinate) [6]. Further studies of these compounds demonstrated facile charge transfer along the Ru_2 -alkynyl backbones [7–9], and a remarkably small attenuation factor (γ) was deduced from the voltammetric and spectroscopic data of the $[\text{Ru}_2(\text{ap})_4]_2(\mu\text{-C}_{2n})$ family with *n* ranging from 1 to 6 [8]. STM (scanning tunneling microscopy) study of $\text{Ru}_2(\text{ap})_4\text{-}\sigma\text{-}[(\text{C}\equiv\text{CC}_6\text{H}_4)_2\text{S}]$ immobilized

on Au surface revealed an improved molecular conductance over $\text{-SC}_6\text{H}_4(\text{C}\equiv\text{CC}_6\text{H}_4)_2\text{S-}$, a conjugated organic molecule of comparable length [10,11]. Despite these successes, the exploration of longer wire-like $\text{Ru}_2(\text{ap})_4$ compounds has been hampered by the poor solubility in common organic solvents [12]. Improved solubility of Ru_2 -alkynyl building blocks may also enable their incorporation into rigid rod polymers with interesting optoelectronic properties [13]. Two *ap*-derivatives, 2-(3-methoxyanilino)pyridinate (MeO*ap*, Chart 1) and 2-(3-propoxyanilino)pyridinate were prepared by us, but only a marginal improvement in solubility was achieved [14]. Described in this contribution are the synthesis and characterization of a new *ap*-derivative, namely 2-(3,5-dimethoxyanilino)pyridine (HDiMeO*ap*, Chart 1) and its Ru_2 -compounds including $\text{Ru}_2(\text{DiMeOap})_4\text{Cl}$ (**1**), $\text{Ru}_2(\text{DiMeOap})_4(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)$ (**2**) and $\text{Ru}_2(\text{DiMeOap})_4(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2$ (**3**). Also reported are the synthesis and characterization of related compounds $\text{Ru}_2(\text{MeOap})_4(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)$ (**4**), $\text{Ru}_2(\text{MeOap})_4(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2$ (**5**), $\text{Ru}_2(\text{MeOap})_4(\text{C}\equiv\text{CFc})$ (**6**) and $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CC}\equiv\text{CFc})$ (**7**).

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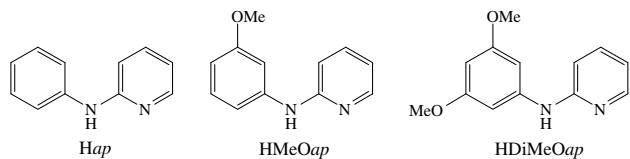


Chart 1.

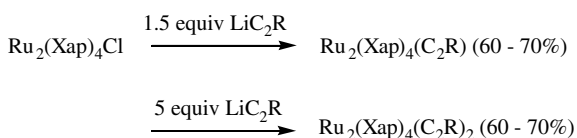
2. Results and discussion

2.1. Synthesis of HDiMeOap, $Ru_2(DiMeOap)_4Cl$ and $Ru_2(Xap)_4(C_2R)_x$ ($x = 1$ or 2)

Ligand HDiMeOap was prepared from the reaction between 2-bromopyridine and 3,5-dimethoxyaniline using a procedure modified from that of HMeOap [14], and was characterized with 1H NMR and mass spectroscopic techniques. Similar to the preparation of $Ru_2(ap)_4Cl$ [4], $Ru_2(DiMeOap)_4Cl$ (**1**) was obtained in satisfactory yield from the reaction of $Ru_2(OAc)_4Cl$ with 7 equiv. of HDiMeOap, and characterized with both the ESI-MS and combustion analysis. Compound **1** has a room temperature effective magnetic moment of 3.89 Bohr magneton, which is consistent with the $S = 3/2$ ground state established early for other $Ru_2(ap)_4Cl$ type compounds [12].

The mono-alkynyl species, namely $Ru_2(DiMeOap)_4(C\equiv CC\equiv CSiMe_3)$ (**2**), $Ru_2(MeOap)_4(C\equiv CC\equiv CSiMe_3)$ (**4**), $Ru_2(MeOap)_4(C\equiv CFC)$ (**6**), and $Ru_2(ap)_4(C\equiv CC\equiv CFC)$ (**7**), were prepared in satisfactory yields from the reaction of $Ru_2(Xap)_4Cl$ with 1.5–2 equiv. of $LiC\equiv CR$ (Scheme 1). Both of the bis-butadiynyl compounds, $Ru_2(DiMeOap)_4(C\equiv CC\equiv CSiMe_3)_2$ (**3**) and $Ru_2(MeOap)_4(C\equiv CC\equiv CSiMe_3)_2$ (**5**), were prepared from the reaction of $Ru_2(Xap)_4Cl$ with ca. 5 equiv of $LiC\equiv CC\equiv CSiMe_3$, which generally resulted in a mixture of the expected bis-compound and the corresponding mono-alkynyl species. Purification via silica column with hexanes/ethyl acetate eluent afforded compounds **3/5** in good yields. Alkynyl compounds supported by both MeOap and DiMeOap ligands are generally more soluble in organic solvents than the *ap*-based alkynyl analogs, and the improved solubility enables more efficient column purification and subsequent characterizations.

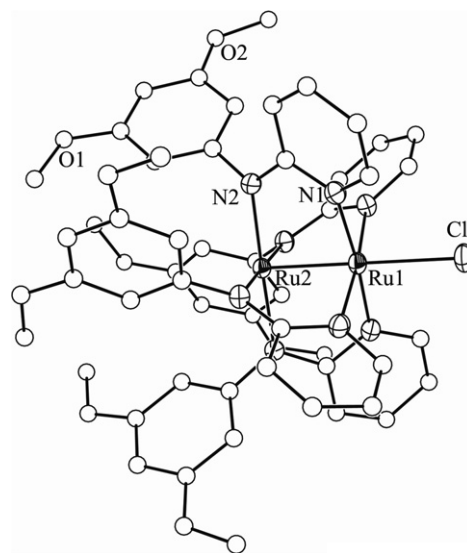
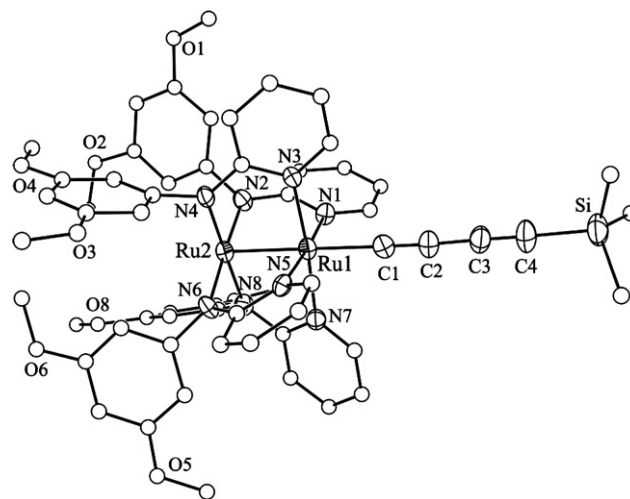
The effective magnetic moments of mono-alkynyl species (**2**, **4** and **6**) range from 3.91 to 4.11 Bohr magneton, which are consistent with an $S = 3/2$ ground state. Compound **7**, on the other hand, exhibits a smaller effective moment. This deviation is not well understood at the moment. Both bis-alkynyl species **3** and **5** are diamagnetic

Scheme 1. Preparation of $Ru_2(Xap)_4(C_2R)_x$ ($x = 1$ and 2).

and display well resolved 1H NMR spectra. All compounds reported herein yielded satisfactory combustion analysis results.

2.2. Structural study

Molecular structures of **1**, **2**, **6** and **7** were established through single crystal X-ray diffraction studies. The structural plots of molecules **1**, **2**, **6** and **7** are shown in Figs. 1–4, respectively, and the selected metric parameters are collected in Table 1. Despite the crowding due to the MeO substituents, the DiMeOap ligands in **1** adopt the so-called (4,0) arrangement similar to $Ru_2(ap)_4Cl$ [15], where all pyridine nitrogens coordinate to the Ru(III) (Ru1), and all aniline nitrogens coordinate to the other Ru (Ru2).

Fig. 1. Structural plot of compound **1** at 30% probability level. Hydrogen atoms were omitted for clarity.Fig. 2. Structural plot of compound **2** at 30% probability level. Hydrogen atoms were omitted for clarity.

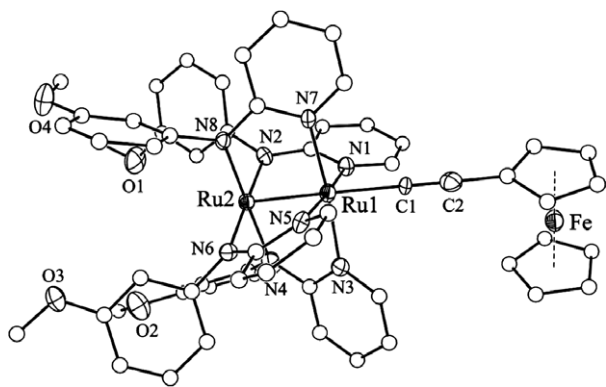


Fig. 3. Structural plot of molecule **6** at 30% probability level. Hydrogen atoms were omitted for clarity.

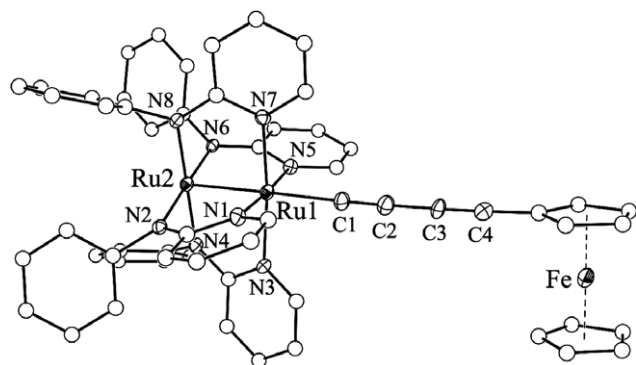


Fig. 4. Structural plot of molecule **7** at 30% probability level. Hydrogen atoms were omitted for clarity.

The Ru–Ru bond length in **1** is 2.2797(7) Å, identical to that of Ru₂(*ap*)₄Cl (2.275(3) Å) within the experimental errors. Compound **1** was crystallized in the *P4/n* space group and the Ru₂–Ru₁–Cl vector coincides with a crystallographic 4-fold axis. There is a significant difference between two independent Ru–N bond lengths: 2.094(3) Å for Ru₁–N₁ and 2.039(3) Å for Ru₂–N₂. The difference is attributed to the fact that the anilino nitrogen is a better donor than the pyridino nitrogen.

The resemblance between molecule **2** and its precursor molecule **1** is clear from Figs. 1 and 2. The notable differences include the displacement of the axial chloro ligand in **1** by the butadiynyl ligand in **2** and the loss of crystallographic symmetry in the latter compound. The Ru–Ru bond length in **2** (2.3245(6) Å) is significantly elongated from that of **1** because of the strong σ -donating ability of the butadiynyl ligand. Both the Ru–C (2.089(6) Å) and C≡C (1.210(7) Å) bond lengths agree well with those previously reported for Ru₂(*ap*)₄(C₂R) type compounds [12,16]. Structural similarity among mono-alkynyl compounds **2**, **6** and **7** is also apparent from the comparison of Figs. 2–4 and geometric parameters listed in Table 1. In addition, they have nearly identical Ru–Ru bond lengths, indicating the comparable donor strengths of *ap*, *MeOap* and *DiMeOap* ligands despite the difference in aniline ring substituents.

2.3. Electrochemistry and spectroscopy

Similar to the previously reported Ru₂(*ap*)₄L_{*x*} (*x* = 1 and 2) type compounds, compounds **1–7** exhibit rich redox activities and both the cyclic (CV) and differential pulse (DPV)

Table 1
Selected bond lengths (Å) and angles (°) for compounds **1**, **2**, **6** and **7**

	1		2		6		7
Ru ₂ –Ru ₁	2.2797(7)	Ru ₂ –Ru ₁	2.3245(6)	Ru ₂ –Ru ₁	2.3223(6)	Ru ₂ –Ru ₁	2.3282(7)
Ru ₁ –Cl	2.459(2)	Ru ₁ –C ₁	2.089(6)	Ru ₁ –C ₁	2.110(5)	Ru ₁ –C ₁	2.090(6)
Ru ₁ –N ₁	2.094(3)	Ru ₁ –N ₁	2.105(4)	Ru ₁ –N ₁	2.112(5)	Ru ₁ –N ₁	2.090(5)
Ru ₂ –N ₂	2.039(3)	Ru ₁ –N ₃	2.086(4)	Ru ₁ –N ₃	2.097(5)	Ru ₁ –N ₃	2.126(5)
		Ru ₁ –N ₅	2.110(4)	Ru ₁ –N ₅	2.095(5)	Ru ₁ –N ₅	2.115(4)
		Ru ₁ –N ₇	2.099(5)	Ru ₁ –N ₇	2.087(4)	Ru ₁ –N ₇	2.102(5)
		Ru ₂ –N ₂	2.055(4)	Ru ₂ –N ₂	2.035(5)	Ru ₂ –N ₂	2.051(5)
		Ru ₂ –N ₄	2.025(4)	Ru ₂ –N ₄	2.044(4)	Ru ₂ –N ₄	2.043(5)
		Ru ₂ –N ₆	2.037(4)	Ru ₂ –N ₆	2.050(5)	Ru ₂ –N ₆	2.033(4)
		Ru ₂ –N ₈	2.030(4)	Ru ₂ –N ₈	2.040(4)	Ru ₂ –N ₈	2.036(5)
		C ₁ –C ₂	1.210(7)	C ₁ –C ₂	1.180(8)	C ₁ –C ₂	1.195(8)
		C ₂ –C ₃	1.367(8)	C ₂ –C ₃		C ₂ –C ₃	1.402(8)
		C ₃ –C ₄	1.202(8)	C ₃ –C ₄		C ₃ –C ₄	1.197(8)
Ru ₂ –Ru ₁ –Cl	180	Ru ₂ –Ru ₁ –C ₁	179.21(15)	Ru ₂ –Ru ₁ –C ₁	178.04(17)	Ru ₂ –Ru ₁ –C ₁	178.49(19)
Ru ₂ –Ru ₁ –N ₁	87.43(6)	Ru ₂ –Ru ₁ –N ₁	88.88(12)	Ru ₂ –Ru ₁ –N ₁	87.30(13)	Ru ₂ –Ru ₁ –N ₁	88.57(12)
Ru ₁ –Ru ₂ –N ₂	89.24(6)	Ru ₂ –Ru ₁ –N ₃	88.30(12)	Ru ₂ –Ru ₁ –N ₃	87.12(13)	Ru ₂ –Ru ₁ –N ₃	87.20(12)
		Ru ₂ –Ru ₁ –N ₅	86.85(11)	Ru ₂ –Ru ₁ –N ₅	87.87(12)	Ru ₂ –Ru ₁ –N ₅	88.47(12)
		Ru ₂ –Ru ₁ –N ₇	87.25(13)	Ru ₂ –Ru ₁ –N ₇	88.58(12)	Ru ₂ –Ru ₁ –N ₇	88.35(12)
		Ru ₁ –Ru ₂ –N ₂	88.97(12)	Ru ₁ –Ru ₂ –N ₂	89.90(13)	Ru ₁ –Ru ₂ –N ₂	89.05(12)
		Ru ₁ –Ru ₂ –N ₄	88.78(11)	Ru ₁ –Ru ₂ –N ₄	89.94(13)	Ru ₁ –Ru ₂ –N ₄	90.20(12)
		Ru ₁ –Ru ₂ –N ₆	89.16(12)	Ru ₁ –Ru ₂ –N ₆	89.11(13)	Ru ₁ –Ru ₂ –N ₆	90.19(12)
		Ru ₁ –Ru ₂ –N ₈	89.87(13)	Ru ₁ –Ru ₂ –N ₈	89.06(12)	Ru ₁ –Ru ₂ –N ₈	89.64(12)
		Ru ₁ –C ₁ –C ₂	179.2(2)	Ru ₁ –C ₁ –C ₂	178.0(2)	Ru ₁ –C ₁ –C ₂	178.5(2)

voltammograms of compounds **1–3** and **6** are shown in Fig. 5. The Ru₂(II,III) species, namely compounds **1**, **2**, **4**, **6** and **7**, exhibit two reversible one-electron processes, an oxidation (**B**) and a reduction (**C**) as designated in Scheme 2. Consistent with the electron richness at the Ru₂ core, the electrode potentials are most positive (anodic) for compounds with axial chloro ligand and least positive (most cathodic) for compounds with axial ethynyl ligand. Compounds **6** and **7** are also unique in containing ferrocenyl capped ethynyl (**6**) and butadiynyl (**7**) ligands. The Fc⁺/Fc couples are observed at 0.65 and 0.71 V for compounds **6** and **7**, respectively, and the difference in *E*_{1/2} reflects the electron-deficiency of butadiynyl compared to ethynyl. Both the values and the trend of *E*_{1/2}(Fc⁺/Fc) described herein are consistent with those reported for *trans*-Fc(C≡C)_{*n*}-[Ru₂(DMBA)₄](C≡C)_{*m*}Fc (*n*, *m* = 1 and 2) [9].

The bis-alkynyl Ru₂(III,III) species, namely compounds **3** (Fig. 5) and **5**, exhibit two reversible one-electron reductions (**B** and **C**) and an irreversible one-electron oxidation (**A**). The latter feature is in stark contrast with the behavior

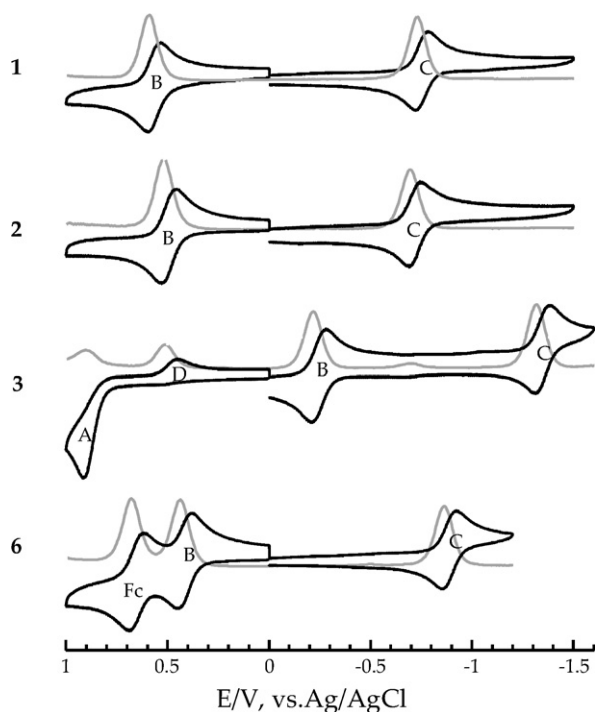
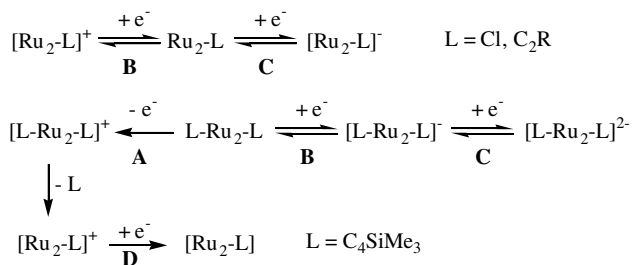


Fig. 5. CV (solid) and DPV (gray) plots of compounds **1–3** and **6**.



Scheme 2. Assignment of redox couples in compounds **1–7**.

of Ru₂(*ap*)₄(C≡CC≡CSiMe₃)₂, which displays a reversible oxidation with *E*_{1/2} of 0.90 V [5]. The irreversible nature of oxidations in **3** and **5** reflects, perhaps, the steric crowding caused by the methoxy substitution of anilino-ring, which drives the molecule to dissociate the butadiynyl ligand on the anilino-side to release the stress on oxidation (Scheme 2). Corroborating this hypothesis, a wave (**D**) was observed for **3** at *E*_{pc} corresponding to the couple **B** of compound **2** and hence the presence of mono-butadiynyl species on the backward sweep of compound **3**.

All Ru₂(*ap*)₄ based compounds are deeply colored. The Ru₂(II,III) species exhibit two intense peaks in the visible region, one at round 800 nm and the other around 450 nm. Upon the formation of bis-alkynyl compounds (Ru₂(III,III)), the absorption profile is altered and further intensified, with peaks around 660 and 500 nm in the visible region, and a very broad and intense peak around 1050 nm. The latter feature, corresponding to a remarkably small optical gap of 1.20 eV, is common among Ru₂(III,III) compounds supported by the *ap*-type ligands [12].

3. Conclusions

Results presented herein describe a significant improvement in organic solubility of Ru₂-alkynyl species through the modification of *ap* ligand without compromising the attractive structural and electronic properties of the original Ru₂(*ap*)₄ compounds. These new Ru₂ building blocks may enable us to access both the Ru₂-(C≡C)_{2*n*}-Ru₂ type compounds with *n* beyond 4 and Ru₂-(C≡C)_{*m*}-Ru₂ type compounds with *m* being odd based on the Glaser type coupling reactions [8,17]. The improved solubility will also facilitate the incorporation of Ru₂-alkynyl species into various device platforms, which offer new opportunities in organometallics based molecular electronics [10,12,18].

4. Experimental

4.1. General

3,5-Dimethoxyaniline and 2-bromopyridine were purchased from ACROS. *n*-BuLi was from Aldrich. 1,3-Bis(trimethylsilyl)butadiyne was from GFS. Ru₂(OAc)₄Cl [19], Ru₂(MeO*ap*)₄Cl [14], FcC≡CH [20] and FcC≡CC≡CH [21] were prepared using the literature reported procedures. THF was distilled over Na/benzophenone under an N₂ atmosphere prior to use. ¹H spectra were recorded on a Varian 300 NMR spectrometer, with chemical shifts (δ) referenced to the residual CHCl₃ and the solvent CDCl₃, respectively. UV-Vis-NIR spectra were obtained in THF with a JASCO V-670 UV-Vis-NIR spectrophotometer. Magnetic susceptibility data were measured at 293 K with a Johnson Matthey Mark-I magnetic susceptibility balance. Cyclic voltammograms were recorded in 0.2 M (*n*-Bu)₄NPF₆ solution (THF, N₂-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a Ag/

Table 2
Electrode potentials (V) of all observed redox couples in compounds 1–7

	E_{pa} (A)	$E_{1/2}$ (B)	$E_{1/2}$ (C)	$E_{1/2}$ (Fc)	E_g/V
$Ru_2(mMeOap)_4Cl^a$		0.560	–0.760		1.324
$Ru_2(DiMeOap)_4Cl$ (1)		0.567	–0.750		1.317
$Ru_2(DiMeOap)_4(C_4TMS)$ (2)		0.491	–0.717		1.208
$Ru_2(DiMeOap)_4(C_4TMS)_2$ (3)	0.915	–0.244	–1.348		
$Ru_2(MeOap)_4(C_4TMS)$ (4)		0.500	–0.716		1.216
$Ru_2(MeOap)_4(C_4TMS)_2$ (5)	0.988	–0.254	–1.362		
$Ru_2(MeOap)_4(C_2Fc)$ (6)		0.416	–0.886	0.654	1.302
$Ru_2(ap)_4(C_4Fc)$ (7)		0.479	–0.762	0.707	1.241

^a From Ref. [14].

AgCl reference electrode. The concentration of diruthenium species is always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.591 V (vs. Ag/AgCl) under experimental conditions Table 2.

4.2. Preparation of 2-(3,5-dimethoxyanilino)pyridine (HDiMeOap)

A 50 mL Schlenk flask was charged with 3,5-dimethoxyaniline (5.1 g, 34 mmol) and 2-bromopyridine (2.6 g, 17 mmol) and heated at 140 °C for 20 h. The mixture was neutralized with NaOH(aq), and then extracted with CH_2Cl_2 . After the solvent removal from the organic layer, the residue was recrystallized from CH_2Cl_2 /hexanes to yield the ligand as an off-white solid (3.0 g, 77% based on 2-bromopyridine). Data for HDiMeOap: 1H NMR: 8.21 (*d*, 1H, aromatic), 7.53–6.17 (*m*, 6H, aromatic), 3.79 (*s*, 6H, OCH_3); MS-ESI: 230 [M^+]; UV–Vis, λ_{max} (nm, ϵ ($M^{-1} cm^{-1}$)): 275 (33600), 256 (13300).

4.3. Preparation of $Ru_2(DiMeOap)_4Cl$ (1)

To a 100 mL round bottom flask was added $Ru_2(OAc)_4Cl$ (1.5 g, 2.5 mmol), HDiMeOap (4.3 g, 19 mmol), excess of LiCl, and 60 mL toluene, and a Soxhlet extraction apparatus with a K_2CO_3 -filled glass thimble was mounted atop the flask. The reaction solution was refluxed for 3 days with K_2CO_3 changed daily. After solvent removal, the residue was dissolved in CH_2Cl_2 and filtered. The filtrate was dried and recrystallized from methanol to yield **1** as black powder (2.6 g, 72% based on Ru). Data for **1**: R_f (THF/hexanes/ $Et_3N = 10/30/1$, v/v/v): 0.17. MS-ESI (*m/e*, based on ^{101}Ru): 1155 [M^+]. Anal. Calc. for $C_{52}H_{52}N_8O_8Ru_2$: C, 54.10; H, 4.51; N, 9.71. Found: C, 54.12; H, 4.49; N, 9.79%. UV–Vis, λ_{max} (nm, ϵ ($M^{-1} cm^{-1}$)): 799 (7870), 452 (6690); Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{backward}/i_{forward}$: **A**, 0.567, 0.064, 0.977; **B**, –0.750, 0.059, 0.997; Magnetic (293 K): χ_g , 4.94×10^{-6} esu; $\chi_{mol}(\text{corr})$ 6.44×10^{-3} esu mol $^{-1}$; μ_{eff} (293 K): 3.89 μ_B .

4.4. Preparation of $Ru_2(DiMeOap)_4(C_4SiMe_3)$ (2)

To a 20 mL THF solution containing 0.95 mmol of $Me_3SiC\equiv CC\equiv CSiMe_3$ was added 0.38 mL of *n*-BuLi (2.5 M in hexanes) at liquid nitrogen temperature. The mix-

ture was slowly warmed to room temperature and stirred for another hour to yield an off-white suspension. A portion of the suspension (15 mL) was transferred to a flask containing a THF solution (40 mL) of $Ru_2(DiMeOap)_4Cl$ (0.538 g, 0.46 mmol). The solution color changed from green to brown immediately, and the reaction mixture was stirred for an hour. Removal of the solvents *in vacuo* yielded a brown residue, which was purified on a silica column deactivated by 10% Et_3N in hexanes using a linear gradient of eluents (hexanes/ethyl acetate, 90/10–60/10, v/v) to afford analytically pure **2** (0.372 g, 65% based on Ru). Data for **2**: R_f (THF/hexanes/ $Et_3N = 10/30/1$, v/v/v): 0.31. MS-ESI (*m/e*, based on ^{101}Ru): 1240 [M^+]. Anal. Calc. for $C_{59}H_{61}N_8O_8SiRu_2$: C, 57.14; H, 4.92; N, 8.92. Found: C, 57.35; H, 5.09; N, 9.04%. UV–Vis, λ_{max} (nm, ϵ ($M^{-1} cm^{-1}$)): 785 (6610), 495 (8830). Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{backward}/i_{forward}$: **A**, 0.491, 0.075, 0.949; **B**, –0.717, 0.052, 0.961. Magnetic (293 K): χ_g , 4.87×10^{-6} esu; $\chi_{mol}(\text{corr})$ 6.78×10^{-3} esu mol $^{-1}$; $\mu_{eff} = 3.99 \mu_B$.

4.5. Preparation of $Ru_2(DiMeOap)_4(C_4SiMe_3)_2$ (3)

To a 10 mL THF solution containing 0.37 mmol of $Me_3SiC\equiv CC\equiv CSiMe_3$ was added 0.10 mL of *n*-BuLi (2.5 M in hexanes) at liquid nitrogen temperature. The mixture was slowly warmed to room temperature and stirred for another hour to yield an off-white suspension. The suspension was transferred to a flask containing a 30 mL THF solution of $Ru_2(DiMeOap)_4Cl$ (0.100 g, 0.086 mmol). The solution color changed from dark green to brown immediately, and the reaction mixture was stirred for an hour. Then the mixture was stirring in the air for another hour to yield a blue-purple solution, which was filtered through a silica gel pad (2 cm). Following the solvent removal, the residue was purified on a silica column deactivated by 10% Et_3N in hexanes using a linear gradient of eluents (hexanes/ethyl acetate, 90/10–60/10, v/v) to afford both compounds **3** and **2**. Yields: **3**, 0.072 g (62% based on Ru); **2**, 0.025 g (23% based on Ru); Data for **3**: R_f (THF/hexanes/ $Et_3N = 10/30/1$, v/v/v): 0.43. MS-ESI (*m/e*, based on ^{101}Ru): 1361 [M^+]. Anal. Calc. for $C_{66}H_{70}N_8O_8Si_2Ru_2$: C, 58.24; H, 5.15; N, 8.24. Found: C, 58.32; H, 5.22; N, 8.20%. 1H NMR: 9.04 (*d*, 4H, aromatic), 7.34–6.06 (*m*, 24H, aromatic), 3.46 (*s*, 24H, OCH_3), 0.31 (*s*, 9H, $Si(CH_3)_3$), 0.09 (*s*, 9H, $Si(CH_3)_3$). UV–Vis, λ_{max} (nm, ϵ

($\text{M}^{-1} \text{cm}^{-1}$): 1049 (7310), 658 (11400), 499 (7780); Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{\text{backward}}/i_{\text{forward}}$: **A**, 0.915 (E_{pa}); **B**, -0.244 , 0.070, 1.057; **C**, -1.348 , 0.068, 0.810.

4.6. Preparation of $\text{Ru}_2(\text{MeOap})_4(\text{C}_4\text{SiMe}_3)$ (**4**)

To a 10 mL THF solution containing 0.16 mmol of $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ was added 0.06 mL of *n*-BuLi (2.5 M in hexanes) at liquid nitrogen temperature. The mixture was slowly warmed to room temperature and stirred for another hour to yield an off-white suspension. A portion of the suspension (6 mL) was transferred to a flask containing a 30 mL THF solution of $\text{Ru}_2(\text{MeOap})_4\text{Cl}$ (0.083 g, 0.08 mmol). The solution color changed from green to brown immediately, and the reaction mixture was stirred for an hour. Removal of the solvents *in vacuo* yielded a brown residue, which was purified on a silica column using a linear gradient of eluents (hexanes/ethyl acetate, 90/10–60/10, v/v) to afford pure **4** (0.055 g, 61% based on Ru). Data for **4**: R_f (THF/hexanes/ $\text{Et}_3\text{N} = 10/30/1$, v/v/v): 0.44. MS-ESI (m/e , based on ^{101}Ru): 1121 [M^+]. UV-Vis, λ_{max} (nm, ϵ ($\text{M}^{-1} \text{cm}^{-1}$)): 770 (7540), 493 (10200). Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{\text{backward}}/i_{\text{forward}}$: **B**, 0.500, 0.067, 0.939; **C**, -0.716 , 0.057, 0.922. Magnetic (293 K): $\mu_{\text{eff}} = 3.91 \mu_{\text{B}}$.

4.7. Preparation of $\text{Ru}_2(\text{MeOap})_4(\text{C}_4\text{SiMe}_3)_2$ (**5**)

To a 10 mL THF solution containing 0.30 mmol of $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ was added 0.15 mL of *n*-BuLi (2.5 M in hexanes) at liquid nitrogen temperature. The mixture was slowly warmed to room temperature and stirred for another hour to yield an off-white suspension. The suspension was transferred to a flask containing a 40 mL THF solution of $\text{Ru}_2(\text{MeOap})_4\text{Cl}$ (0.061 g, 0.058 mmol). After 30 min, the reaction mixture was opened in the air with stirring for another hour to yield a blue-purple solution, which was filtered through a silica gel pad (2 cm). After the solvent removal, the residue was purified on a silica column with hexanes/ethyl acetate (90/10, v/v) to afford **5** (0.050 g, 69% based on Ru). Data for **5**: R_f (THF/hexanes/ $\text{Et}_3\text{N} = 10/30/1$, v/v/v): 0.60. Anal. Calc. for $\text{C}_{62}\text{H}_{62}\text{N}_8\text{O}_4\text{Si}_2\text{Ru}_2 \cdot \text{H}_2\text{O}$: C, 59.07; H, 5.08; N, 8.89. Found: C, 59.05; H, 5.47; N, 8.41%. ^1H NMR: 9.04 (s, 4H, aromatic), 7.25–6.02 (m, 24H, aromatic), 3.42 (s, 12H, OCH_3), 0.29 (s, 9H, Si(CH_3)), 0.08 (s, 9H, Si(CH_3)). Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{\text{backward}}/i_{\text{forward}}$: **A**, 0.988 (E_{pa}); **B**, -0.254 , 0.066, 1.019; **C**, -1.362 , 0.087, 1.109. UV-Vis, λ_{max} (nm, ϵ ($\text{M}^{-1} \text{cm}^{-1}$)): 657 (11400), 486 (7270).

4.8. Preparation of $\text{Ru}_2(\text{MeOap})_4(\text{C}_2\text{Fc})$ (**6**)

To a 40 mL THF solution containing 0.10 mmol of FcC_2H was added 0.05 mL of *n*-BuLi (2.5 M in hexanes) at liquid nitrogen temperature. The mixture was slowly

warmed to room temperature and stirred for another hour. The suspension was transferred to a flask containing a THF solution (40 mL) of $\text{Ru}_2(\text{MeOap})_4\text{Cl}$ (0.085 g, 0.08 mmol). The solution color changed from dark green to red immediately, and the reaction mixture was stirred for 30 min. After the removal of the solvents under vacuum, the residue was dissolved in THF and filtered through a silica gel pad (2 cm). The product was further purified on silica column eluted with a mixture of THF, hexanes and Et_3N (10/30/1, v/v/v) to give pure compound **6** (0.070 g, 72%). Data for **6**: R_f (THF/hexanes/ $\text{Et}_3\text{N} = 10/30/1$, v/v/v): 0.42. MS-ESI (m/e , based on ^{101}Ru): 1210 [M^+]. Anal. Calc. for $\text{C}_{60}\text{H}_{53}\text{N}_8\text{O}_4\text{FeRu}_2$, C, 59.65; H, 4.39; N, 9.28. Found: C, 59.69; H, 4.44; N, 9.05%. UV-Vis, λ_{max} (nm, ϵ ($\text{M}^{-1} \text{cm}^{-1}$)): 753 (5450), 473 (7850); Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{\text{backward}}/i_{\text{forward}}$: **A**, 0.654, 0.072, 1.102; **B**, 0.416, 0.069, 0.715; **C**, -0.886 , 0.071, 0.922. Magnetic (293 K): χ_{g} , 5.34×10^{-6} esu; $\chi_{\text{mol}}(\text{corr})$ 7.20×10^{-3} esu mol $^{-1}$; $\mu_{\text{eff}} = 4.11 \mu_{\text{B}}$.

4.9. Preparation of $\text{Ru}_2(\text{ap})_4(\text{C}_4\text{Fc})$ (**7**)

To a 20 mL THF solution containing 0.37 mmol of FcC_4H was added 0.16 mL of *n*-BuLi (2.5 M in hexanes) at liquid nitrogen temperature. The mixture was slowly warmed to room temperature and stirred for another hour. The suspension was transferred to a flask containing a THF solution (40 mL) of $\text{Ru}_2(\text{ap})_4\text{Cl}$ (0.229 g, 0.25 mmol). The solution color changed from dark green to red immediately, and the reaction mixture was stirred for 30 min. After the removal of the solvents under vacuum, the residue was dissolved in THF and filtered through a silica gel pad (2 cm). The product was further purified on silica column with a mixture of THF, hexanes and Et_3N (25/100/1, v/v/v) to yield pure compound **7** (0.098 g, 35%). Data for **7**: R_f (THF/hexanes/ $\text{Et}_3\text{N} = 10/30/1$, v/v/v): 0.66. MS-ESI (m/e , based on ^{101}Ru): 1112 [M^+]. Anal. Calc. for $\text{C}_{58}\text{H}_{45}\text{N}_8\text{FeRu}_2 \cdot 2\text{H}_2\text{O}$: C, 60.63; H, 4.27; N, 9.65. Found: C, 60.37; H, 4.70; N, 9.72%. UV-Vis, λ_{max} (nm, ϵ ($\text{M}^{-1} \text{cm}^{-1}$)): 755 (7640), 473 (8260). Electrochemistry (THF), $E_{1/2}/V$, $\Delta E_p/V$, $i_{\text{backward}}/i_{\text{forward}}$: **A**, 0.707, 0.040, 0.280; **B**, 0.479, 0.060, 0.556; **C**, -0.762 , 0.068, 0.923. Magnetic (294 K): χ_{g} , 3.77×10^{-6} esu; $\chi_{\text{mol}}(\text{corr})$ 4.95×10^{-3} esu mol $^{-1}$; $\mu_{\text{eff}} = 3.41 \mu_{\text{B}}$.

4.10. Structure determination

Single crystals were obtained by slow evaporation of either a hexanes/THF solution (**1**, **6** and **7**) or a hexanes/ethyl acetate solution (**2**). X-ray intensity data of crystals **1**, **2** and **6** were measured on a Bruker SMART1000 CCD X-ray diffractometer and those of **7** on a Nonius-Kappa CCD X-ray diffractometer using Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$). Structures were solved and refined using the Bruker SHELXTL© (Version 5.1) software package. Positions of all non-hydrogen atoms were revealed by direct method. The asymmetric unit of crystal **1** contains one-

Table 3
Crystal data for compounds **1**, **2**, **6** and **7**

	1 · 2THF	(2) ₂ · EtOAc	6 · THF	7 · THF
Formula	C ₆₀ H ₆₈ ClN ₈ O ₁₀ Ru ₂	C ₁₂₂ H ₁₂₂ N ₁₆ O ₁₆ Ru ₄	C ₆₄ H ₆₁ FeN ₈ O ₅ Ru ₂	C ₆₂ H ₅₃ FeN ₈ ORu ₂
FW	1106.57	2358.68	1280.20	1184.15
Space group	<i>P</i> 4/ <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.377(1)	13.956(1)	17.397(1)	10.125(2)
<i>b</i> (Å)	13.377(1)	20.943(1)	10.2286(6)	13.667(2)
<i>c</i> (Å)	16.723(2)	22.34(1)	32.822(2)	19.620(3)
α (°)		89.700(1)		72.81(8)
β (°)		73.637(1)	102.394(1)	78.83(8)
γ (°)		81.980(1)		85.84(8)
<i>V</i> (Å ³)	2992.6(4)	6198.7(6)	5704.6(6)	2544.2(7)
<i>Z</i>	2	2	4	2
ρ_{calc} (g cm ⁻³)	1.441	1.264	1.491	1.546
μ (mm ⁻¹)	0.613	0.332	0.832	0.907
Crystal size (mm)	0.35 × 0.27 × 0.06	0.25 × 0.21 × 0.03	0.24 × 0.09 × 0.04	0.25 × 0.19 × 0.05
Unique reflections (<i>R</i> _{int})	2652 (0.029)	21579 (0.039)	10012 (0.067)	10299 (0.095)
Parameters refined	175	1459	700	667
<i>T</i> (K)	300	300	300	150
<i>R</i> , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.035, 0.094	0.054, 0.110	0.052, 0.106	0.061, 0.128
Goodness-of-fit on <i>F</i> ²	1.05	1.01	1.00	1.04

quarter of the molecule, which is related to the rest of the molecule via a crystallographic fourfold axis coinciding with the Ru–Ru vector, and one-half of a THF molecule. The asymmetric unit of crystal **2** contains two independent diruthenium molecule and one ethyl acetate solvent. Each of the asymmetric units of crystals **6** and **7** contains one complete diruthenium molecule and a THF molecule. 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.

5. Supplementary material

CCDC 666214, 666215, 666216 and 666217 contain the supplementary crystallographic data for this paper. 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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