# Synthesis and Dynamic Behavior of an Anthyridine-Ligated Ruthenium Complex

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**S** *Supporting Information*

**ABSTRACT:** A ruthenium complex containing a 1,9,10-anthyridine derivative, $[Ru(L)(bpy)_2](PF_6)_2$ ($[1](PF_6)_2$; L = 1,13,14-triazadibenz[$a,j$]anthracene, bpy = 2,2′-bipyridyl), was synthesized. X-ray crystal structural analysis of $[1](PF_6)_2$ showed that L is coordinated to the Ru center as a bidentate ligand. When $[1](PF_6)_2$ was dissolved in acetonitrile, a new complex incorporating one acetonitrile molecule, $[Ru(L)(CH_3CN)(bpy)_2](PF_6)_2$ ($[2](PF_6)_2$), was formed. X-ray crystallographic data revealed that, in $[2](PF_6)_2$, L is coordinated to the Ru center in a monodentate fashion. The coordinated L in $[2](PF_6)_2$ shows a unique haptotropic rearrangement in an acetonitrile solution.

Transition-metal complexes that exhibit dynamic behavior such as reversible metal migration on a ligand have attracted much attention for applications in dynamic molecular devices and switches.[1] Several examples of metal migration over ligands that possess multiple binding sites, as a result of oxidation–reduction of the metal center[2] or acid/base treatment of the ligand,[3] have been reported. A ligand such as 1,8-naphthyridine (napy), with a 1,8-diazine structure, can coordinate with a metal center through both N atoms to form a four-membered ring.[4,5] Such a structure can undergo large distortions, and, consequently, the bidentate coordination mode can be converted to the monodentate form by treatment with another ligand such as acetonitrile, as shown in Scheme 1a.[4d] In addition, complexes of napy and its analogues can undergo intramolecular 1,3 shifts of the metal, known as "1,3-haptotropic shifts" (Scheme 1b).[6]

**Scheme 1. Dynamic Behavior of a napy Ligand Coordinated to a Transition Metal M: (a) Change of the Coordination Mode; (b) 1,3-Haptotropic Shift**
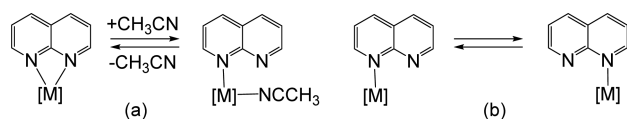


1,9,10-Anthyridine (anth), which has a pyridine-fused 1,8-napy structure, is also expected to show interesting dynamic behavior such as changes in the coordination mode (monodentate–bidentate) and long-range migration when it is coordinated to a transition metal. Although there are a few reports on anth-ligated transition-metal complexes,[7] no research regarding the dynamic behavior of the anth ligand in such complexes has been pursued, to the best of our knowledge.

In this paper, we report the first synthesis of a ruthenium complex with an anth-based ligand. We also explore the unique dynamic behavior of the complex, i.e., long-range reversible migration of the $[Ru(bpy)_2]$ unit between positions 1 and 14 of the N atom (the numbering of L is shown in Scheme 2) in a $CH_3CN$ solution.

**Scheme 2. Synthesis of $[1](PF_6)_2$**
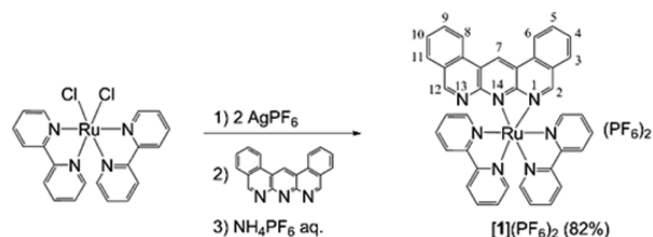


The synthetically accessible anth derivative, 1,13,14-triazadibenz[$a,j$]anthracene (L), was prepared according to a previous report.[8] The anth-ligated ruthenium complex $[Ru(L)-(bpy)_2](PF_6)_2$ ($[1](PF_6)_2$; L = 1,13,14-triazadibenz[$a,j$]-anthracene, bpy = 2,2′-bipyridyl) was synthesized by the reaction of $AgPF_6$-treated $[RuCl_2(bpy)_2]$ with L in 2-methoxyethanol in 82% yield (Scheme 2).

The electrospray ionization mass spectrometry spectrum of $[1](PF_6)_2$ in acetone shows a parent peak at $m/z$ 347.55 as a dication pattern (Figure S1 in the Supporting Information, SI). Figure 1a depicts the molecular structure of $[1]^{2+}$ determined by X-ray crystallography. In $[1]^{2+}$, L is coordinated to the Ru center
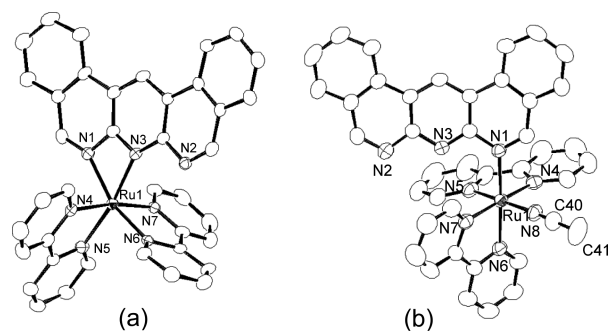


**Figure 1.** ORTEP drawings of the cationic parts of (a) $[1](PF_6)_2$ and (b) $[2](PF_6)_2$. H atoms are omitted for clarity.

by two N atoms, and the N1−Ru1−N3 angle is 63.30(11)°. The Ru1−N1 and Ru1−N3 bond lengths are 2.133(2) and 2.089(3) Å, respectively, which are similar to the Ru−N(napy) bond length in $[Ru(napy)(bpy)_2]^{2+}$ [2.11(1) Å].[4d] The Ru1−N1 bond is longer than the Ru1−N3 bond because of the steric repulsion between L and the bpy ligands.

In the $^1H$ NMR spectrum of $[1](PF_6)_2$ in acetone-$d_6$, three characteristic singlet peaks are observed at $\delta$ 9.76 (H$^a$), 9.31 (H$^b$), and 10.85 (H$^c$) (Figure S2a in the SI). The former two are assigned to the protons situated ortho to the N atoms, at the 2 and 12 positions of L, and the latter is assigned to the proton at the 7 position of L. The appearance of inequivalent H$^a$ and H$^b$ strongly suggests that the L ligand in $[1](PF_6)_2$ is ligated to the Ru center in a bidentate fashion in an acetone solution. The spectrum of $[1](PF_6)_2$ was not changed when the complex was heated in an acetone solution to 55 °C. This result suggests that L in $[1](PF_6)_2$ does not show dynamic behavior in acetone. An acetone solution of $[1](PF_6)_2$ has a reddish-brown color. In contrast, a $CH_3CN$ solution of $[1](PF_6)_2$ is yellow.

The UV−vis spectra of $[1](PF_6)_2$ in acetone and $CH_3CN$ are shown in Figure S3 in the SI. $[1](PF_6)_2$ exhibits absorbance peaks at 515, 455, and 287 nm in an acetone solution. The absorption bands observed at lower energy are assigned to metal-to-ligand charge transfer (MLCT) transitions. On the other hand, in the UV−vis spectrum of $[1](PF_6)_2$ in $CH_3CN$, an MLCT absorption was observed at 430 nm, and the absorption bands observed at longer wavelengths in acetone disappeared. These results strongly indicate that the coordination environment of the anth ligand was changed dramatically. Such a color change was also observed for the Ru-napy complex $[Ru(napy)(bpy)_2]$-$(PF_6)_2$.[4d] To isolate the new species that is generated in $CH_3CN$, $[1](PF_6)_2$ was recrystallized from a $CH_3CN$ solution. Figure 1b shows the ORTEP drawing of the cationic part of $[1](PF_6)_2$ recrystallized from $CH_3CN$−$Et_2O$ ($[Ru(L)(CH_3CN)(bpy)_2]$-$(PF_6)_2$ ($[2](PF_6)_2$)). One $CH_3CN$ molecule is coordinated to the Ru center, and the coordination mode of L is changed from bidentate to monodentate. The Ru1−N1 bond length is 2.148(4) Å, which is greater than that in $[Ru(napy)(CH_3CN)(bpy)_2]^{2+}$ ($[3]^{2+}$).[4d] The uncoordinated pyrido moiety of L in the complex is oriented toward the bpy ligand, which is different from $[3]^{2+}$, due to the steric repulsion between L and the coordinated $CH_3CN$ ligand. The $^1H$ NMR spectrum of complex $[2](PF_6)_2$ in $CH_3CN$ shows three characteristic singlet peaks originating from the L ligand at $\delta$ 10.30, 10.09 and 9.52, which are assigned to the protons at the 7, 2, and 12 positions of L, respectively (Figure S2b in the SI). In addition, small signals attributable to $[1](PF_6)_2$ are also observed. These results suggest that the coordinated $CH_3CN$ in $[2](PF_6)_2$ is dissociable and the monodentate complex is in equilibrium with $[1](PF_6)_2$ in $CH_3CN$ (Scheme 3).

To clarify the dynamic behavior of $[1](PF_6)_2$, $^1H$ NMR spectral analyses were carried out. Variable-temperature (VT) $^1H$ NMR spectra of $[1](PF_6)_2$ in $CD_3CN$ are shown in Figure 2. The major species in solution at −35 °C is $[2](PF_6)_2$ ($K_a = 35.5$).

## Scheme 3. Changes of the Coordination Mode of L





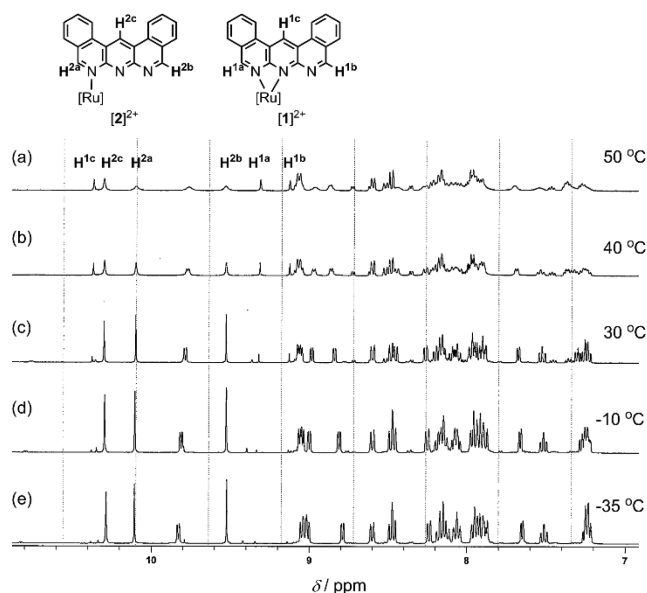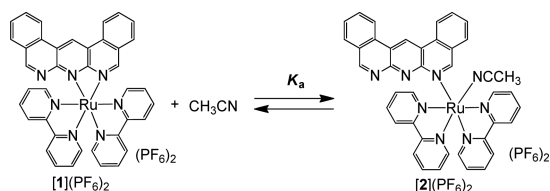**Figure 2.** VT $^1H$ NMR spectra of $[1](PF_6)_2$ in $CD_3CN$ at (a) +50, (b) +40, (c) +30, (d) −10, and (e) −35 °C.

When the temperature is increased, the amount of $[1](PF_6)_2$ is increased[9] and the peak shapes are broadened gradually. At 50 °C, the $K_a$ value is 1.7. The temperature dependence of the equilibrium constants gives the apparent thermodynamic parameters of the reaction: $\Delta H° = -30.6$ kJ mol$^{-1}$ and $\Delta S° = -89.6$ J mol$^{-1}$ K$^{-1}$ (Figure S4 in the SI). In contrast, the VT $^1H$ NMR spectra of $[1](PF_6)_2$ in acetone-$d_6$ show almost no change in the region of −40 to +50 °C, suggesting that $[1](PF_6)_2$ does not show dynamic behavior in noncoordinating solvents.

From X-ray analysis, L in $[2](PF_6)_2$ is coordinated to the Ru center by a terminal N atom. If the coordinated L can show dynamic behavior such as reversible metal migration, the metal would be expected to move over the three N atoms freely. To determine the dynamic behavior of $[2](PF_6)_2$ in more detail, a 1D exchange spectroscopy (EXSY) $^1H$ NMR technique was used. When the peak at $\delta$ 9.53 was irradiated, the intensity of the resonance at $\delta$ 10.10 was decreased. In addition, the two singlet peaks observed at $\delta$ 9.1 and 9.3, which are assigned to the anth protons in the bidentate anth-ligated ruthenium complex, showed such a relationship under the irradiation conditions (Figure S5 in the SI). This result strongly suggests that the anth ligand in $[2](PF_6)_2$ shows dynamic behavior in $CH_3CN$. From these results, plausible site-exchange pathways of the reaction can be considered (Scheme 4). **A** is in equilibrium with **B** in $CH_3CN$. When an acetonitrile molecule is coordinated to the Ru center of **B**, two possible structures can result. If the Ru−N2 bond is cleaved, **A** is regenerated. On the other hand, if the Ru−N1 bond is cleaved, another monodentate L-ligated species, **C**, may be produced. **C** can be converted to **E** in a manner similar to the conversion of **C** to **A**.

Previously, the dynamic behavior of transition-metal napy complexes in solution has been reported. In $[3]^{2+}$, the Ru-coordinated napy ligand in a monodentate fashion, undergoes a 1,3-haptotropic shift in $CH_3CN$. The shift is very fast, and therefore the exchange rate could not be estimated from $^1H$ NMR spectral analyses of $[3]^{2+}$. In contrast to $[3]^{2+}$, the haptotropic shift of the anth ligand occurs more slowly than that of a napy ligand, which may be caused by the difference in basicity of the N atoms in L. Because the N atom at the 14 position of L

**Scheme 4. Plausible Dynamic Processes for L Coordinated to Ru**
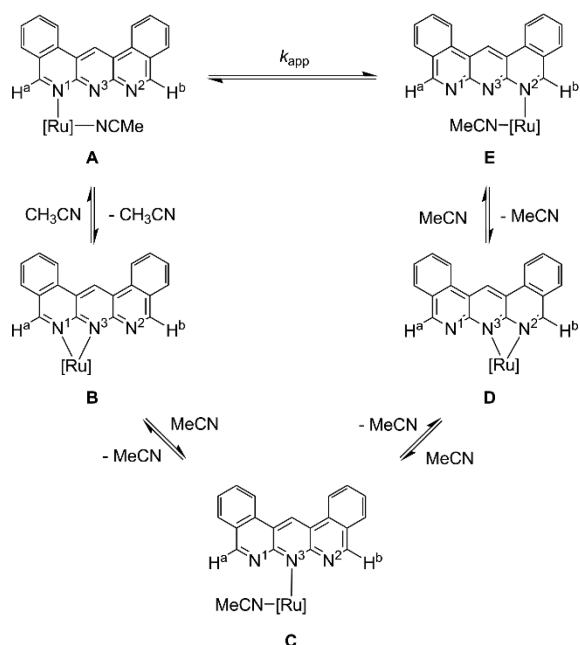


(N3 in Scheme 4) is situated between two electron-withdrawing imine N atoms (N1 and N2 in Scheme 4), its coordination ability toward the Ru is lower than that of N1 and N2. Therefore, because conversion of **B** to **C** (or **D** to **C**) in Scheme 4 is less favored, the exchange of **A** and **E** is slowed.

In summary, we synthesized a new ruthenium complex having an anth-derived ligand, $[1](PF_6)_2$, and elucidated the dynamic behavior of the complex in acetonitrile. $[1](PF_6)_2$ is converted to $[2](PF_6)_2$ by treatment with acetonitrile. From the VT and EXSY $^1$H NMR analyses, $[2](PF_6)_2$ exhibits characteristic dynamic behaviors such as the change of the coordination mode of **L** and long-range metal migration. The dynamic behavior of the anth ligand in transition-metal complexes is expected to be applicable in the development of molecular motion devices and switches.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information
X-ray crystallographic data of $[1](PF_6)_2$ (CCDC 100411) and $[2](PF_6)_3 \cdot 3CH_3CN$ (100412) in CIF format, experimental details, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes
The authors declare no competing financial interest.

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(9) Because $[1]^{2+}$ has a Ru−N−C−N four-membered structure, the distortion of the structure is very large. Therefore, it is considered that $[2]^{2+}$ is more stable than $[1]^{2+}$ thermodynamically. The $\Delta H°$ value ($-30.6$ kJ mol$^{-1}$) supports this fact. On the other hand, in this case, both the $\Delta H°$ and $\Delta S°$ values are minus ($-30.6$ kJ mol$^{-1}$ and $-89.6$ J mol$^{-1}$ K$^{-1}$, respectively). In such a case, at high temperature, because the entropy term ($T\Delta S$) is dominant, the backward reaction ($[1]^{2+} + CH_3CN \leftarrow [2]^{2+}$) is superior. Therefore, formation of $[2]^{2+}$ is predominant at low temperature, and the formation of $[1]^{2+}$ becomes superior as the temperature increases.