

## Synthesis and Characterization of Ruthenium(II)–Nitrile Complexes with Bisamide-tpa Ligands (tpa = Tris(2-pyridylmethyl)amine)

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Ruthenium(II)–acetonitrile complexes having pentadentate tris(2-pyridylmethyl)amine (tpa) derivatives with coordinated amide CO groups were prepared and characterized by various spectroscopic methods, electrochemical measurements, and DFT calculations. The acetonitrile ligand was indicated to tightly bind to the ruthenium(II) center in an  $\eta^1$ -N fashion. The Mulliken charge distribution, obtained by a calculation, indicated that the ruthenium(II)–nitrile bond is more covalent than other coordination bonds of the tpa moiety. The redox potentials of Ru centers and the chemical shifts of methyl groups of the acetonitrile ligands exhibited a linear relationship, indicating that electron density of the Ru center controls that of the acetonitrile ligand. Those complexes showed fluxional behavior in CD<sub>3</sub>CN solutions to exhibit one mode of thermal motion; it also altered the symmetry of the complexes.

Transition-metal complexes having organonitriles have been recognized to be reactive intermediates toward nucleophilic reactions due to  $\sigma$ -donation of the non-bonding lone pair to electron-deficient metal centers in an  $\eta^1$ -N monodentate fashion, accompanied by reduction of the electron density at the C $\equiv$ N moiety.<sup>1,2</sup> For example, those  $\eta^1$ -nitrile ligands can be converted to amides via the hydration to nitrile C $\equiv$ N triple bonds.<sup>3</sup> In addition, a cationic [RuCp(acetonitrile)]<sup>+</sup> has been shown to perform catalytic cyclotrimerization of alkynes to afford benzene derivatives.<sup>4</sup> On the contrary, the nitriles coordinated to electron-rich and  $\pi$ -donating metal complexes are expected to exhibit reactivity toward electrophiles owing to their  $\pi$ -accepting character. Thus, the electron density of the metal center can regulate the reactivity of those coordinated nitriles. As ligands, organonitriles have been classified to be moderate  $\sigma$ -donors and  $\pi$ -acceptors toward transition metals. The ordering of  $\pi$ -acceptor character was examined by using Mössbauer<sup>5</sup> and IR<sup>6</sup> spectroscopies to demonstrate that the  $\pi$ -acceptor character of the nitriles is less than that of N<sub>2</sub> and more than that of pyridine.

Since the ruthenium(II) ion has the d<sup>6</sup> low-spin configuration, and is classified to be a moderately soft acid based on the Hard–Soft Acid–Base (HSAB) theory,<sup>7</sup> it has an ability to donate the d $\pi$  electron to a coordinated  $\pi$ -acceptor. Thus, the coordination of nitriles to ruthenium(II) centers should be attributable to not only  $\sigma$ -donation of the lone pair of the nitrile ligand to the ruthenium(II) center, but  $\pi$ -back donation from the d $\pi$  orbital of ruthenium(II) to the  $\pi^*$  orbital of the nitrile.

We have reported on the synthesis and reactivity of ruthenium complexes having tris(2-pyridylmethyl)amine (tpa) and its derivatives as ligands.<sup>8</sup> In the course of our research on Ru–tpa complexes having two naphthoylamide groups at the 6-positions of two pyridine rings in tpa, we found that intramolecular hydrogen bonding is indispensable to construct and stabilize specific coordination environments.<sup>9</sup> Masuda and co-workers have also reported on the synthesis and characterization of similar ruthenium complexes, involving their application toward hydrocarbon oxidations.<sup>10</sup>

We have focused on the role of the intramolecular hydrogen bonding to regulate the reactivity and property of the ruthenium center. We have proposed that the hydrogen bonding could enrich the electron density at the ruthenium center. Thus, we chose acetonitrile as a ligand to estimate the  $\pi$ -back bonding from the ruthenium center to the ligand by spectroscopic and electrochemical methods. In this article, we describe the synthesis and characterization of ruthenium(II)–acetonitrile complexes with the use of spectroscopic methods, including EXAFS analysis, electrochemical measurements, and DFT calculations.

### Experimental

**Materials.** Precursor complexes, [RuCl(1-Naph<sub>2</sub>-tpa)]PF<sub>6</sub> (1-Naph<sub>2</sub>-tpa = *N,N*-bis(6-(1-naphthoylamide)-2-pyridylmethyl)-*N*-(2-pyridylmethyl)amine) (**1**), [RuCl(2-Naph<sub>2</sub>-tpa)]PF<sub>6</sub> (2-Naph<sub>2</sub>-tpa = *N,N*-bis(6-(2-naphthoylamide)-2-pyridylmethyl)-*N*-(2-pyridylmethyl)amine) (**2**), and [RuCl(isob<sub>2</sub>-tpa)]PF<sub>6</sub> (isob<sub>2</sub>-tpa = *N,N*-bis(6-(isobutyrylamide)-2-pyridylmethyl)-*N*-(2-pyridylmethyl)amine) (**3**) were prepared as reported.<sup>8</sup> CH<sub>3</sub>CN was dried on CaH<sub>2</sub> and then distilled under N<sub>2</sub> and stored on a Molecular Sieves 3A. All other reagents were of analytical and/or reagent

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grade and used without further purification.

**Instrumentation.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on JEOL GX-400 and/or EX-270 spectrometers.  $^1\text{H}$ – $^{13}\text{C}$  HMBC spectra were recorded on a JEOL  $\alpha$ -600 spectrometer. Chemical shifts were determined relative to residual solvent peaks. UV–vis absorption spectra were measured in  $\text{CH}_3\text{CN}$  on a Jasco Ubest-55 UV–vis spectrophotometer at room temperature. Infrared spectra were recorded as KBr disks in the range of 4000–400  $\text{cm}^{-1}$  on a Jasco IR model 800 infrared spectrophotometer. ESI-MS spectra were obtained on a Perkin-Elmer Sciex API-300 mass spectrometer. FAB-MS spectra were measured on a JMS-SX/SX102A Tandem Mass spectrometer.

Cyclic voltammograms were recorded on a HECS 312B dc pulse polarograph (Fuso Electrochemical System) attached to a HECS 321B potential-sweep unit of the same manufacture, and an electrochemical analyzer, Model 720 (ALS/chi). A glassy carbon (3 mm o.d.) was employed as a working electrode, a platinum coil as a counter electrode, and a silver/silver nitrate ( $\text{Ag}/\text{AgNO}_3$ ) electrode as a reference electrode, respectively. All measurements were carried out in  $\text{CH}_3\text{CN}$  containing 0.1 M  $[(n\text{-Bu})_4\text{N}]\text{ClO}_4$  as a supporting electrolyte under  $\text{N}_2$  at ambient temperatures. The redox potentials were determined relative to a ferrocene/ferrocenium couple as a reference (0 V).

Elemental analysis data for all compounds were obtained at the Service Center of the Elemental Analysis of Organic Compounds, Department of Chemistry, Kyushu University.

**EXAFS Measurements.** Ru K-edge X-ray absorption experiments were carried out on a BLOB1 beam-line of SPring-8 (Hyogo, Japan). Spectra were collected in the transmission mode. Solid samples (0.1 g) were mixed and grinded with boron nitride (0.5 g) and pressed to disks of 0.5 cmf. Curve-fitting analysis of the EXAFS spectra was performed on the inversely Fourier transformed radial distribution function, and was made by using the FEFFIT program.

**Synthesis of  $[\text{Ru}(\text{1-Naph}_2\text{-tpa})(\text{CH}_3\text{CN})](\text{PF}_6)_2 \cdot 1/2\text{CH}_3\text{CN}$  (4).**  $\text{AgNO}_3$  (47.6 mg, 0.280 mmol) was added to a red solution of  $[\text{RuCl}(\text{1-Naph}_2\text{-tpa})]\text{PF}_6$  (1) (200 mg, 0.215 mmol) in  $\text{CH}_3\text{CN}$  (40 mL). The mixture was refluxed for 4 h and the color turned to be orange; a white precipitate of  $\text{AgCl}$  was observed. After removing the precipitate by filtration, the filtrate was dried up under reduced pressure. The residue was dissolved into a small volume of acetone/EtOH, and then  $\text{NH}_4\text{PF}_6$  (40 mg, 0.239 mmol) was added as solids. The mixture was concentrated to a small volume to obtain a brown precipitate. The precipitate was filtered and washed with a small volume of EtOH, followed by  $\text{Et}_2\text{O}$ , and then dried in vacuo to obtain the brown powder of **1** in 84% yield (178 mg). Anal. Calcd for  $\text{C}_{42}\text{H}_{35}\text{N}_7\text{O}_2\text{RuP}_2\text{F}_{12} \cdot 1/2\text{CH}_3\text{CN}$ : C, 47.76; H, 3.40; N, 9.72%. Found: C, 47.80; H, 3.39; N, 9.64%. ESI-MS: 770.2,  $\{[\text{Ru}(\text{1-Naph}_2\text{-tpa})(\text{CH}_3\text{CN})\text{-H}]^+\}$ ; 916.3,  $\{[\text{Ru}(\text{1-Naph}_2\text{-tpa})(\text{CH}_3\text{CN})]\text{PF}_6\}^+$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.39 (3H, s,  $\text{CH}_3$ ), 4.39 and 4.58 (2H, ABq,  $J = 18$  Hz,  $\text{CH}_2$ ), 4.81 and 4.85 (2H, ABq,  $J = 16$  Hz,  $\text{CH}_2$ ), 4.91 (2H, pseudo-s,  $\text{CH}_2$ ), 6.42 (1H, dd,  $J = 8$  and 7 Hz, 1-Naph-H6), 6.9–8.0 (multiplets, aromatic), 8.25 (1H, d,  $J = 5$  Hz, py-H6), 8.54 (1H, d,  $J = 8$  Hz, 1-Naph-H2), 9.84 (1H, brs, amide-NH, uncoordinated), 12.04 (ca. 1H, brs, amide-NH).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  131.3 (CN).

**Synthesis of  $[\text{Ru}(\text{2-Naph}_2\text{-tpa})(\text{CH}_3\text{CN})](\text{PF}_6)_2 \cdot \text{H}_2\text{O} \cdot 1/2\text{CH}_3\text{CN}$  (5· $\text{H}_2\text{O} \cdot 1/2\text{CH}_3\text{CN}$ ) and  $[\text{Ru}(\text{isob}_2\text{-tpa})(\text{CH}_3\text{CN})](\text{PF}_6)_2 \cdot 1.5\text{H}_2\text{O}$  (6· $1.5\text{H}_2\text{O}$ ).** These complexes were prepared by the same procedure as described for **4**, except  $[\text{RuCl}(\text{2-Naph}_2\text{-tpa})]\text{PF}_6$  (**2**) and  $[\text{RuCl}(\text{isob}_2\text{-tpa})]\text{PF}_6$  (**3**) were used as the starting materials, respectively. Elemental analysis

gave satisfactory results. For **5**: Anal. Calcd for  $\text{C}_{42}\text{H}_{35}\text{N}_7\text{O}_2 \cdot \text{P}_2\text{F}_{12}\text{Ru} \cdot \text{H}_2\text{O} \cdot 1/2\text{CH}_3\text{CN}$  (**5**· $\text{H}_2\text{O} \cdot 1/2\text{CH}_3\text{CN}$ ): C, 46.98; H, 3.53; N, 9.56%. Found: C, 47.18; H, 3.42; N, 9.75%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.34 (3H, s,  $\text{CH}_3$ ), 4.39 and 4.58 (2H, ABq,  $J = 18$  Hz,  $\text{CH}_2$ ), 4.82 and 4.85 (2H, ABq,  $J = 18$  Hz,  $\text{CH}_2$ ), 4.91 (2H, s,  $\text{CH}_2$ ), 7.0–8.2 (multiplets, aromatic).

For **6**: Anal. Calcd for  $\text{C}_{28}\text{H}_{35}\text{N}_7\text{O}_2\text{P}_2\text{F}_{12}\text{Ru} \cdot 1.5\text{H}_2\text{O}$  (**6**· $1.5\text{H}_2\text{O}$ ): C, 36.57; H, 4.16; N, 10.66%. Found: C, 36.27; H, 3.94; N, 11.03%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  1.18, 1.28, 1.38, and 1.47 (for all; 3H, d,  $J = 7$  Hz,  $\text{CH}_3$  of isob), 2.31 (3H, s,  $\text{CH}_3$  of  $\text{CH}_3\text{CN}$ ), 2.80 and 3.13 (1H, 7-tet,  $J = 7$  Hz, CH of isob), 4.13 and 4.58 (2H, ABq,  $J = 18$  Hz,  $\text{CH}_2$ ), 4.74 (2H, s,  $\text{CH}_2$ ), 4.78 (2H, s,  $\text{CH}_2$ ), 7.11–7.27 (multiplets, aromatic).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  181.2 and 176.4 (CO of amide), 162.6, 162.0, 157.8, 149.9, 140.2, 139.4, 138.3, 130.6 (CN of  $\text{CH}_3\text{CN}$ ), 125.1, 121.8, 118.8, 118.6, 116.2, 115.5 (pyr of tpa), 70.5, 70.4, 68.8 ( $-\text{CH}_2-$ ), 38.3, 37.5 (CH of isob), 19.83, 19.77, 19.5, 19.1 ( $\text{CH}_3$  of isob), 4.7 ( $\text{CH}_3$  of  $\text{CH}_3\text{CN}$ ).

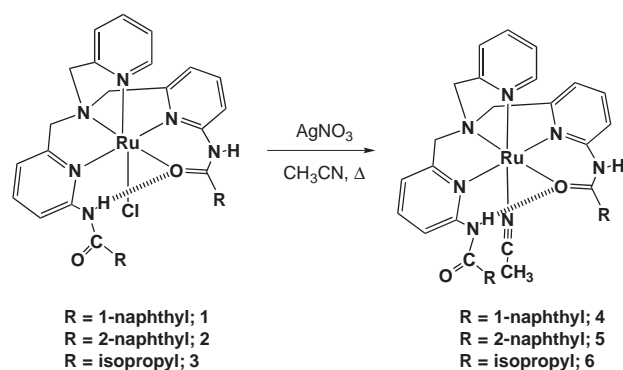
**DFT Calculations.** We optimized the geometry of a model complex,  $\{[\text{Ru}(\text{bis}(\text{acetoamide})\text{-tpa})(\text{CH}_3\text{CN})]\text{Cl}\}^+$ , which was constructed based on the crystal structure of **1**, using the B3LYP method,<sup>11</sup> which has been reported to provide excellent descriptions of various reaction profiles, particularly concerning geometries, heats of reaction, barrier heights, and vibrational analyses. For the Ru atom we used Los Alamos ECP with double- $\zeta$  basis,<sup>12</sup> and for the H, C, O, and N atoms we used the D95 basis set,<sup>13</sup> a standard double-z basis.

## Results and Discussion

**Synthesis of Nitrile Complexes.** We established the crystal structures of the precursors  $[\text{RuCl}(\text{1-Naph}_2\text{-tpa})](\text{PF}_6)$  (**1**),<sup>9</sup>  $[\text{RuCl}(\text{2-Naph}_2\text{-tpa})](\text{PF}_6)$  (**2**),<sup>9</sup> and  $[\text{RuCl}(\text{isob}_2\text{-tpa})]\text{PF}_6$  (**3**)<sup>9</sup> to reveal one amide oxygen coordinated to the ruthenium center. It bound to the uncoordinated amide NH via an intramolecular hydrogen bonding.

Acetonitrile complexes  $[\text{Ru}(\text{1-Naph}_2\text{-tpa})(\text{CH}_3\text{CN})](\text{PF}_6)_2$  (**4**),  $[\text{Ru}(\text{2-Naph}_2\text{-tpa})(\text{CH}_3\text{CN})](\text{PF}_6)_2$  (**5**), and  $[\text{Ru}(\text{isob}_2\text{-tpa})(\text{CH}_3\text{CN})](\text{PF}_6)_2$  (**6**) were synthesized in good yields by treating **1–3** with  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$  to remove the chloride ligands (Scheme 1).<sup>14</sup> In the course of the reaction, the red color of the chloride complexes turned to be brown, and the LMCT band from  $\text{Cl}^-$  to ruthenium(II) around 430 nm disappeared. The products were characterized by means of elemental analysis, ESI-MS, IR, NMR, and EXAFS spectroscopies, and also electrochemical measurements.

Concerning the ESI-MS spectrum of **4**, peaks assigned to



Scheme 1. Synthesis of acetonitrile complexes.

Table 1. Spectroscopic Data for Acetonitrile Complexes

Complex	$\nu(\text{CN})^{\text{a)}}$ / $\text{cm}^{-1}$	$\delta(^{13}\text{C}/\text{CN})^{\text{b)}}$	$\delta(^1\text{H}/\text{CH}_3)^{\text{c)}}$
<b>4</b>	2268 (2220) <sup>d)</sup>	131.3	2.39
<b>5</b>	— <sup>e)</sup>	— <sup>f)</sup>	2.34
<b>6</b>	2251	130.6	2.31
[Ru(TPA)(bpy)(CH <sub>3</sub> CN)](PF <sub>6</sub> ) <sub>2</sub> <sup>g)</sup>	2266	— <sup>f)</sup>	2.45 <sup>h)</sup>

a) Data obtained by KBr method. b) In CD<sub>2</sub>Cl<sub>2</sub>. c) In CD<sub>3</sub>CN. d) Synthesized with use of CH<sub>3</sub><sup>13</sup>CN. e) Too weak to be observed. f) Not available. g) See Ref. 4g. h) In CD<sub>3</sub>OD.

{[Ru(1-Naph<sub>2</sub>-tpa)(CH<sub>3</sub>CN)]-H}<sup>+</sup> at 770.2 and those of {[Ru(1-Naph<sub>2</sub>-tpa)(CH<sub>3</sub>CN)](PF<sub>6</sub>)<sup>+</sup> at 916.3 in addition to those of {[Ru(1-Naph<sub>2</sub>-tpa)(CH<sub>3</sub>CN)]<sup>2+</sup> at 385.5 were observed and their isotopic patterns were consistent with their computer simulations. Complex **5** also showed the same spectral pattern as **4**. These complexes have a tetradentate tpa ligand and concomitant coordination of one of the amide oxygen, as discussed below.

**Spectroscopic Characterization.** Representative spectroscopic data are summarized in Table 1. In the IR spectra of **4** and **6** (KBr method), very weak absorption due to  $\nu(\text{CN})$  were observed at 2268 and 2251 cm<sup>-1</sup>, respectively, which were slightly higher than those of free nitriles (2200–2240 cm<sup>-1</sup>). This difference between **4** and **6** may be derived from electronic effects of the substituents; the isopropyl groups are more electron-donating than the 1-naphthyl groups as reflected on the redox potentials of **1** and **3**. This more electron-donating character renders the ruthenium center to be more electron-rich to facilitate  $\pi$ -back bonding toward the C $\equiv$ N moiety. The  $\nu(\text{CN})$  for **5** was not clearly determined due to the weakness of the peak. An isotope shift was observed for **4** by using CH<sub>3</sub><sup>13</sup>CN, and  $\nu(\text{CN})$  was shifted to 2220 cm<sup>-1</sup> ( $\Delta\nu = 48$  cm<sup>-1</sup>), which exhibited excellent agreement with the calculated value. It is known that the  $\eta^1$ -coordination of nitriles is usually accompanied by an increase in  $\nu(\text{CN})$ ,<sup>15</sup> although in several cases it has been found to remain virtually unchanged, or at lower frequencies than those of free nitriles, due to significant back-bonding from the d $\pi$  orbitals of electron-rich metal centers to the  $\pi^*$  orbitals of the nitriles.<sup>16</sup> In our cases, the ruthenium(II) centers undergo sufficient electron donation from the pentadentate tpa ligands to be electron-rich and  $\pi$ -back bonding from the metal center can be facilitated toward the acetonitrile ligands, which are the strongest  $\pi$ -acceptor in those complexes, to give a relatively small increase of  $\nu(\text{CN})$ .

In the <sup>1</sup>H NMR spectra of acetonitrile complexes, singlets ascribed to the methyl groups of the coordinated acetonitriles were observed at 2.39 ppm for **4**, 2.34 ppm for **5**, and 2.31 ppm for **6** in CD<sub>3</sub>CN at room temperature without any remarkable exchange with the deuterated solvent. This observation suggests that the acetonitrile ligand binds tightly to the ruthenium(II) center.<sup>17</sup> Those chemical shifts exhibited a good linear relationship with their redox potentials of Ru<sup>II</sup>/Ru<sup>III</sup> couples of the corresponding precursor complexes **1–3**, as shown in Fig. 1, indicating the more electron-rich is the ruthenium center, the more does the  $\pi$ -back donation occur toward  $\pi^*$  orbital of the nitrile. The chemical shifts showed slight downfield shifts compared to those of  $\eta^1$ -coordinated acetonitrile

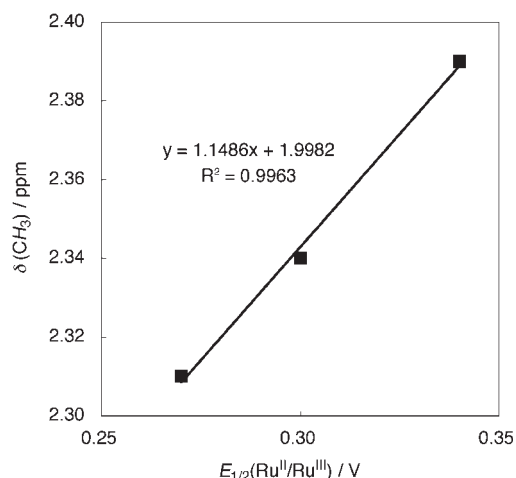


Fig. 1. Relationship between redox potentials of **1–3** and the chemical shifts of the methyl groups of the acetonitrile ligands of **4–6**.

trile (2.1 ppm) and upfield shifts relative to those of  $\eta^2$ -coordination (>3 ppm).<sup>18</sup> In addition, the upfield shift in the chemical shifts of the methyl group of the acetonitrile ligand in **3** compared to that of **1** corresponds to the lower energy shift of  $\nu(\text{CN})$  in **3**, suggesting that the electron density at the ruthenium center can be transferred to the acetonitrile ligand.

In the <sup>13</sup>C NMR spectrum of **4**, a peak due to C $\equiv$ N was observed at 131.3 ppm in CD<sub>2</sub>Cl<sub>2</sub>. As for that of **6**, a peak assigned to the methyl group of CH<sub>3</sub>CN ligand was observed at 4.72 ppm, and that of C $\equiv$ N was observed at 130.6 ppm, which was assigned by <sup>1</sup>H-<sup>13</sup>C HMBBC spectroscopy (Figure S1 in Supporting Information). Based on IR and <sup>13</sup>C NMR spectroscopic data, the coordination mode of the acetonitrile ligand in **4–6** is a usual  $\eta^1$ -N fashion.

In CD<sub>3</sub>CN, resonances due to the methylene groups of the tpa ligand in **4** were observed as an AB quartet at 4.39 and 4.58 ppm ( $J_{\text{AB}} = 18$  Hz), pseudo-AB quartet at 4.81 and 4.85 ppm ( $J_{\text{AB}} = 16$  Hz), and a pseudo-singlet at 4.91 ppm at room temperature. This multiplicity indicates that one amide oxygen atom still binds to the ruthenium(II) center to hold an asymmetric coordination environment, as found in the precursor.<sup>9</sup> These signals showed a temperature dependency of multiplicity and other peaks also showed a temperature-dependent change of those chemical shifts in variable-temperature <sup>1</sup>H NMR spectroscopy in CD<sub>3</sub>CN in the range from -40 to 50 °C, as shown in Fig. 2.

As for **6**, its <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN exhibited two apparent singlets and one AB quartet for the methylene moieties

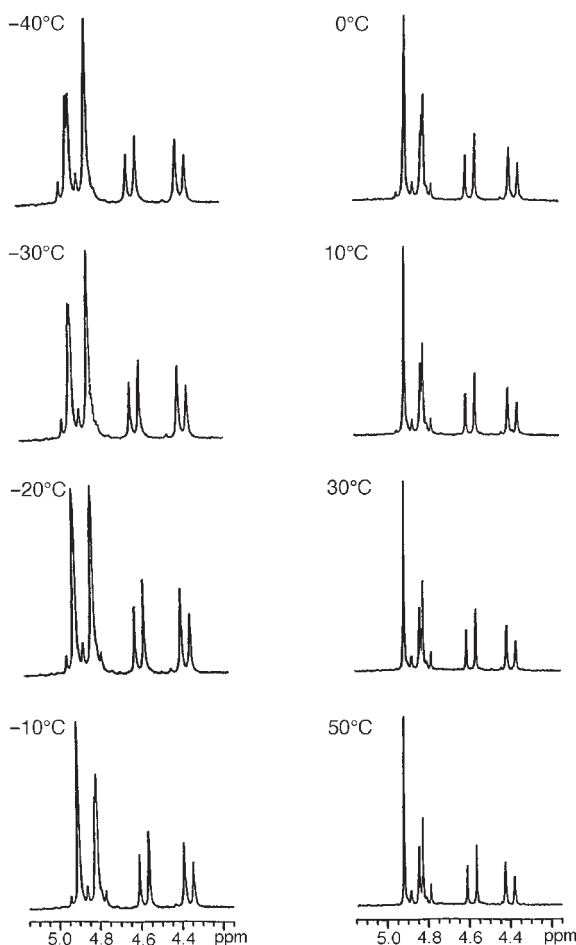


Fig. 2. VT  $^1\text{H}$ NMR spectra of **4** (methylene region) in  $\text{CD}_3\text{CN}$ .

of isob<sub>2</sub>-tpa. In acetone-*d*<sub>6</sub>, however, the spectrum showed three AB quartets at room temperature: one was observed at 4.66 and 4.90 ppm ( $J_{\text{AB}} = 18$  Hz), the other two overlapped at 5.07–5.22 ppm with  $J_{\text{AB}} = 15$  and 16 Hz. Also, broad singlets due to amide N–H protons were observed at 9.28 (br) and 11.4 ppm (very broad); the former peak should be ascribed to the uncoordinated amide moiety with hydrogen bonding, and the latter should be assigned to the coordinated amide group. These results were almost identical to those of **4** (see Experimental section). The higher positive charge of the ruthenium center renders the coordinated amide N–H more acidic than that in **3**. These observations suggest that the complexes have a similar geometry to those of **1–3**, possessing coordinated amide moieties without any symmetric plane.

Interestingly, the singlet assigned to the methyl group of the coordinated acetonitrile showed a temperature dependence in its chemical shift. The singlet exhibited upfield shifts upon cooling. In all cases of the three complexes, the chemical shifts of the methyl groups and that of the CN carbon (for **4**) of coordinated acetonitrile showed a nice linear relationship with  $1/T$ , as depicted in Figs. 3 and 4, respectively. These observations indicate that only one mode of fluxional behavior is considered to alter the symmetry of the complexes. However, we cannot describe the detailed picture of the motion at this point, unfortunately. Also, the coordination environment of the ace-

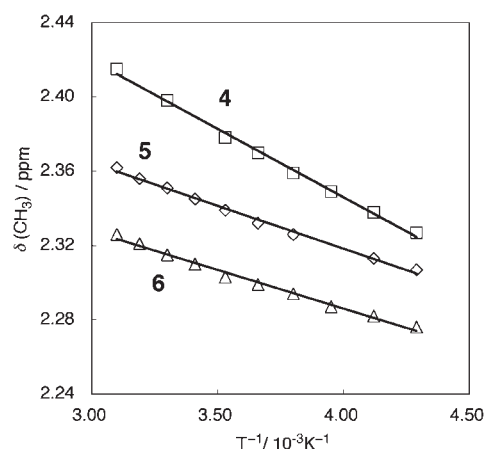


Fig. 3. Temperature-dependence of chemical shifts of the methyl groups in **4–6** in  $\text{CD}_3\text{CN}$ .

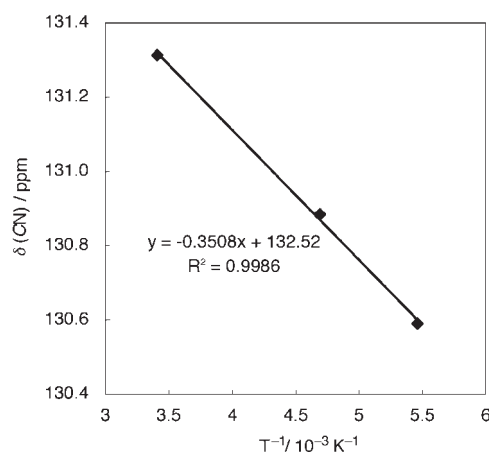


Fig. 4. Temperature-dependence of the chemical shifts of  $\text{CH}_3^{13}\text{C}$  N in  $^{13}\text{C}$  NMR spectra of **4** in  $\text{CD}_2\text{Cl}_2$ .

tonitrile ligands of those complexes should be similar, as judged from those chemical shifts and the fluxional behavior. As for the thermal motion of acetonitrile ligands, it could be derived from the thermal vibration of the ligand in the coordination spheres of those ruthenium(II) complexes. At lower temperatures, the vibration could be retarded and  $\pi$ -back donation from  $d\pi$  of the ruthenium(II) center to  $p\pi^*$  of the acetonitrile ligand would be facilitated to make it electron-rich and cause the observed upfield shifts.

Concerning the existence of the intramolecular hydrogen bonding between the coordinated amide oxygen and the uncoordinated N–H group, we measured the temperature dependence of the chemical shifts of one broad singlet observed for **4** in  $\text{CD}_3\text{CN}$ , which could be assigned to the uncoordinated N–H group. As shown in Fig. S3 (Supporting Information), the gradient of the linear relationship was determined to be 1.4 ppb/K, which was comparable to that (1 ppb/K)<sup>5</sup> of **1**. This clearly indicates that intramolecular hydrogen bonding is operating in the acetonitrile complexes discussed here.

**EXAFS Analysis of the Nitrile Complexes.** In order to accumulate structural information, we also examined EXAFS spectroscopy to argue the coordination mode of the acetonitrile ligand of **4–6**.<sup>19</sup> Curve fittings of EXAFS data used a model



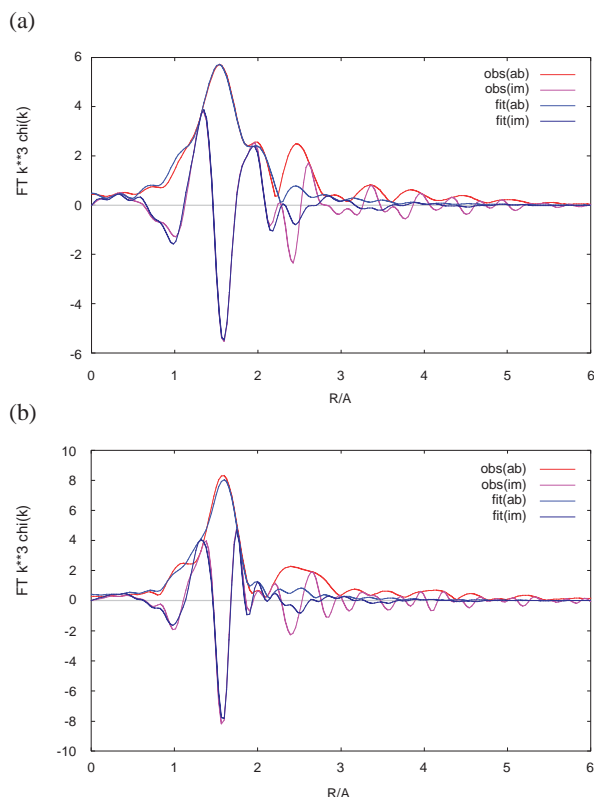
Fig. 5. Curve-fittings of EXAFS analysis for **1** (a) and **4** (b).

Table 2. Curve-Fitting Results of EXAFS of Ru Complexes

Ru complexes	Ru–O/N		Ru–Cl		<i>R</i> /%
	<i>r</i> /Å	<i>N</i>	<i>r</i> /Å	<i>N</i>	
<b>1</b>	2.08	6.0	2.40	1.3	0.59
<b>2</b>	2.06	5.2	2.45	0.8	1.49
<b>3</b>	2.06	4.8	2.45	1.2	0.45
<b>4</b>	2.06	5.9			2.02
<b>5</b>	2.06	5.3			3.64
<b>6</b>	2.06	5.9			1.55

with DFT-generated geometry, which was based on the crystal structure of **1**. The radial distribution functions (RDF) for **1** and **4** are presented in Fig. 5, in which the red lines are the observed spectra and the blue lines are simulated curves.<sup>20</sup> Curve-fitting results for six complexes are summarized in Table 2.

The EXAFS spectra of **1–3** gave the distances of 2.40–2.45 Å for Ru–Cl distances, showing good agreement with crystallographic data (2.446(2) Å for **1**, 2.4351(9) Å for **2**, and 2.437(1) Å for **3**). As for the CH<sub>3</sub>CN complexes **4–6**, the corresponding Ru–Cl absorptions disappeared. The pre-edge features of **4–6** were almost identical to those of **1–3**, indicating that the oxidation state of the ruthenium centers in CH<sub>3</sub>CN complexes was intact to be divalent (+2). The bond distances around the ruthenium center were estimated 2.055 Å in a single shell. Curve fittings for **5** and **6** gave similar bond distances of 2.057 and 2.061 Å, respectively.

X-ray crystallography on **1–3** has revealed that the bond lengths around the ruthenium centers deviate in the range

Table 3. Redox Potentials of Complexes **1–6** in CH<sub>3</sub>CN

Complex	<i>E</i> <sub>1/2</sub> (V) <sup>a)</sup>
[RuCl(1-Naph <sub>2</sub> -tpa)]PF <sub>6</sub> ( <b>1</b> )	0.34 <sup>b)</sup>
[RuCl(2-Naph <sub>2</sub> -tpa)]PF <sub>6</sub> ( <b>2</b> )	0.30 <sup>b)</sup>
[RuCl(isob <sub>2</sub> -tpa)]PF <sub>6</sub> ( <b>3</b> )	0.27 <sup>b)</sup>
[Ru(CH <sub>3</sub> CN)(1-Naph <sub>2</sub> -tpa)](PF <sub>6</sub> ) <sub>2</sub> ( <b>4</b> )	0.86
[Ru(CH <sub>3</sub> CN)(2-Naph <sub>2</sub> -tpa)](PF <sub>6</sub> ) <sub>2</sub> ( <b>5</b> )	0.82
[Ru(CH <sub>3</sub> CN)(isob <sub>2</sub> -tpa)](PF <sub>6</sub> ) <sub>2</sub> ( <b>6</b> )	0.83
[Ru(3-Me <sub>3</sub> -tpa) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	0.67 <sup>c)</sup>

a) Potentials were determined relative to that of Fc/Fc<sup>+</sup> redox couple as a reference (0 V). b) See Ref. 5. c) T. Kojima, unpublished result. See Ref. 8e.

of 2.125–1.992 Å (average 2.053 Å) for **1**, 2.113–2.005 Å (average 2.067 Å) for **2**, and 2.126–2.011 Å (average 2.068 Å) for **3**. These values are in good agreement with those estimated by EXAFS, as listed in Table 2. Those observations could lend credence to the distances around the ruthenium centers of **4–6**, to be discussed. In the CH<sub>3</sub>CN complexes, the bond distances could be almost the same as in the precursor complexes, except for the loss of those of the Ru–Cl bonds. As for the ruthenium(II)–acetonitrile complexes reported so far, the bond distances of Ru–N(nitrile) have been found to be, for example, 2.032(4) Å for [Ru(2,2′-bipyridine)<sub>2</sub>(PhCN)](PF<sub>6</sub>)<sub>2</sub>,<sup>21</sup> 2.041(5) Å for [Ru(terpy)(bpy)(CH<sub>3</sub>CN)](PF<sub>6</sub>)<sub>2</sub>,<sup>22</sup> 2.050(2) and 2.052(2) Å for [Ru(Cp)(PCy<sub>3</sub>)(CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub>,<sup>23</sup> and 2.165(18) Å for [RuCl<sub>2</sub>(cycloocta-1,5-diene)(CO)].<sup>24</sup> Thus, the bond distance of 2.06 Å in **4–6** is within the range of the Ru–N(NCCH<sub>3</sub>) bond lengths.

**Electrochemical Analysis.** Electrochemical measurements were made by cyclic voltammetry (CV) to determine the redox potentials of **4–6** in CH<sub>3</sub>CN at room temperature in the presence of 0.1 M [(*n*-butyl)<sub>4</sub>N]ClO<sub>4</sub> as an electrolyte. The results are summarized in Table 3. Reversible one-electron redox waves due to Ru<sup>II</sup>/Ru<sup>III</sup> couples were observed at 0.86 V (**4**), 0.82 V (**5**), and 0.83 V (**6**) relative to ferrocene/ferrocenium redox couple as 0 V, respectively. Those potentials were ca. 0.5 V higher than those of **1** (0.34 V), **2** (0.30 V), and **3** (0.27 V). A bis-chelate ruthenium(II) complex of tris(3-methyl-2-pyridylmethyl)amine [Ru(3-Me<sub>3</sub>-tpa)<sub>2</sub>]<sup>2+</sup>,<sup>8e</sup> which has four pyridine groups as  $\pi$ -acceptors and two tertiary amino groups as  $\sigma$ -donors, shows a corresponding Ru<sup>II</sup>/Ru<sup>III</sup> couple at 0.67 V,<sup>25</sup> which is lower than those of **4–6**. Thus, the higher redox potentials of the acetonitrile complexes can be derived from the  $\pi$ -acceptor character of the acetonitrile ligand.

**DFT Calculations.** In order to access the structural features and electronic properties of the Ru–tpa acetonitrile complexes, DFT calculations were performed on a model complex, {[Ru{*N,N*-bis(6-acetoamide-2-pyridylmethyl)-*N*-(2-pyridylmethyl)amine}(CH<sub>3</sub>CN)](Cl<sup>–</sup>)}<sup>+</sup>, which was constructed on the basis of the crystal structure of **1**. In Fig. 6a, we show an optimized structure of the ruthenium(II)–nitrile complex, in which the nitrogen atom of acetonitrile directly coordinates to the ruthenium atom in an  $\eta^1$ -*N* form. In this complex, the four Ru–N(tpa) bond distances are 2.081, 2.085, 2.051, and 2.132 Å, and the Ru–O(amide) bond distance is 2.171 Å. These geometrical parameters are fully consistent with the values estimated from an EXAFS analysis. The Ru–N(nitrile) bond dis-

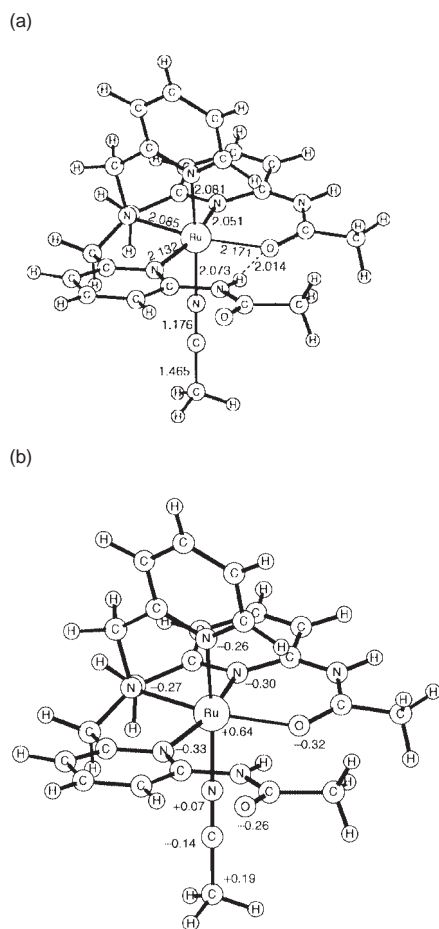
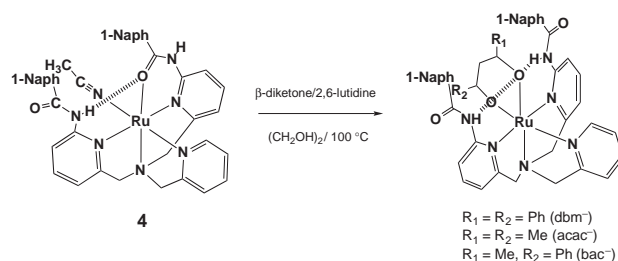


Fig. 6. (a) The optimized structure of the model complex with selected bond lengths (Å) at the B3LYP/LANL2DZ level and (b) Mulliken charges of selected atoms.

tance of 2.073 Å is in good agreement with the results of an EXAFS analysis, and those reported in the literature.<sup>16–19</sup> The oxygen atom coordinating to the ruthenium ion forms a hydrogen bond (2.014 Å) with a neighboring H atom, which anchors the uncoordinated amide group. This hydrogen bond plays an important role in the stability of the Ru–O(amide) coordination bond, since the exchange reaction of the two amide groups requires hydrogen bond breaking to rotate the uncoordinating amide group. The difference between the coordinating and uncoordinating amide groups induces the multiplicity of the methylene groups of the tpa ligand through an asymmetric coordination environment.

In Fig. 6b, computed Mulliken charges of selected atoms are described. The charge of the Ru center is +0.64 and those of the N and O atoms of the pentadentate tpa ligand are all negative in the range of –0.33––0.26. In sharp contrast to those, the acetonitrile ligand has a different charge distribution. The charge of the coordinating N atom is +0.07, which derives from a strong covalent character of Ru–NCCH<sub>3</sub> bonding. In addition, the cyano carbon has a negative charge of –0.14, although the electronegativity of the nitrogen atom (3.0) is larger than that of the carbon atom (2.5).<sup>26</sup> Previously, Cotton proposed that nitriles bound to zero-valent transition-metal complexes show the following resonance structure hybrid:  $\text{C}\equiv\text{N}^+\text{M}^- \leftrightarrow \text{C}^-\text{N}^+=\text{M}$ .<sup>27</sup>



Scheme 2. Formation of  $\beta$ -diketonato complexes.

$\text{N}^+-\text{M}^- \leftrightarrow \text{C}^-\text{N}^+=\text{M}$ .<sup>27</sup> This strong covalent character may stem from a combination of the  $\sigma$ -donation of the lone pair and the  $\pi$ -back bonding from the ruthenium(II) center to the  $\pi^*$  orbitals of the  $\text{C}\equiv\text{N}$  bond.

To estimate the  $\text{C}\equiv\text{N}$  stretching mode of the ruthenium(II)–nitrile complex, we performed a harmonic-frequency analysis using a scaling factor<sup>21</sup> of 0.98. As mentioned above, the ruthenium(II)–nitrile complex has a high  $\text{C}\equiv\text{N}$  stretching mode relative to that in the free acetonitrile. The calculated  $\text{C}\equiv\text{N}$  stretching modes of the ruthenium(II)–nitrile complex and the free acetonitrile are 2256 and 2245  $\text{cm}^{-1}$  at the B3LYP/LANL2DZ level of theory, respectively. This result is fully consistent with a change of the  $\text{C}\equiv\text{N}$  bond distance: 1.176 Å in the ruthenium(II)–nitrile complex and 1.180 Å in the free acetonitrile. The result indicates that the formation of the Ru–N(nitrile) bond should come from the back bonding of the metal center to the  $\pi^*$  orbital of nitrile. The  $\text{C}\equiv\text{N}$  stretching frequency for the ruthenium(II)–nitrile complex is shifted to 2201  $\text{cm}^{-1}$  with  $\text{CH}_3^{13}\text{CN}$  substitution, which is consistent with our experimental observation.

**Reaction of **4** with  $\beta$ -Diketones.** Transition-metal complexes with acetonitrile ligand have been used as starting materials toward further syntheses of coordination compounds.<sup>2</sup> Recently, we reported on the synthesis and characterization of  $\beta$ -diketonato complexes with 1-Naph<sub>2</sub>-tpa as the ligand.<sup>28</sup> Those complexes could be obtained from reactions of **1** with  $\beta$ -diketones. Based on this, we examined the reaction of **4** with  $\beta$ -diketones (acetylacetone (Hacac), dibenzoylmethane (Hdbm), and benzoylacetone (Hbac)) in ethylene glycol in the presence of 2,6-dimethylpyridine (2,6-lutidine) as a base at 100 °C. The reactions gave the corresponding  $\beta$ -diketonato complexes,  $[\text{Ru}(\beta\text{-diketonato})(1\text{-Naph}_2\text{-tpa})]^+$  in similar yields, as shown in Scheme 2. All products were analyzed by <sup>1</sup>H NMR and UV–vis spectroscopies, and those data were consistent with those reported previously. The apparent reaction rates were also similar to those from **1**, suggesting that the acetonitrile binding is as strong as that of a negatively charged chloride anion.

## Summary

We prepared and characterized a series of ruthenium(II)–acetonitrile complexes with bisamide-tpa ligands. A spectroscopic study indicated that those complexes should have the  $\eta^1$ -N acetonitrile ligand and one of amide moieties bound to the ruthenium(II) center through amide oxygen with intramolecular hydrogen bonding with the uncoordinated counterpart. A DFT study on a model complex allowed us to access an optimized structure, which was consistent with other spectro-

scopic data. More importantly, coordination of the acetonitrile ligand is suggested to have a strong covalent character compared with that of the tpa ligands.

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### Supporting Information

HMBC spectrum ( $\text{CD}_3\text{CN}$ ) of **6**, VT  $^1\text{H}$  NMR spectra ( $\text{CD}_3\text{CN}$ ) for **4**, temperature-dependence of the chemical shifts of the NH signal for **4**, and EXAFS spectra (**2**, **3**, **5**, and **6**) (PDF).

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