Ruthenium(II) Complexes Having a Pincer Type Ligand with Two N Heterocyclic Carbene Moieties

Ruthenium(II) Complexes Having a Pincer-Type Ligand with Two *N*-Heterocyclic Carbene Moieties
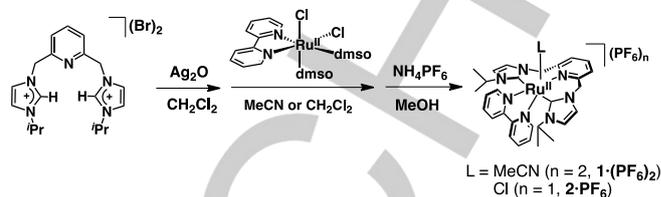
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Abstract: Two novel Ru(II) complexes, having 2,2'-bipyridyl and a pincer-type methylene-bridged *N*-heterocyclic carbene (NHC) ligand, have been synthesized and characterized to evaluate the effects of structural features of the complexes on their redox and photochemical properties. The methylene-bridged NHC ligand coordinated in a meridional manner and the *iso*-propyl groups on the NHC rings exhibited intramolecular CH/π interaction with the 2,2'-bipyridyl ligand, which played a role to strongly maintain the distorted ligand structure. In addition, the two Ru complexes exhibited reversible redox waves in the cyclic voltammograms and they were oxidized by an electron-transfer oxidant to afford Ru(III) complexes, which were characterized by ESR spectroscopy and theoretical analyses.

Transition-metal complexes bearing *N*-heterocyclic carbene (NHC) ligands have been widely studied for several decades.[1] In particular, 4d transition metals are capable of forming highly stable coordination bonds with NHC ligands and they have been widely applied to construction of catalytic systems.[2] Among them, Ru(II) and Ru(III) complexes having NHC ligands have been applied to catalysis such as substrate oxidation[3] and water oxidation,[4] and they also have gathered much attention to the photochemical properties.[5] For example, the strong coordination of an NHC ligand to a Ru(II) center allowed us to elongate the lifetime of the excited state related to the emission, compared to its polypyridyl analogs.[5] Although plenty of reports on Ru-NHC complexes have been delivered, the effects of NHC ligands on the electronic structures of Ru-NHC complexes have been scarcely reported.[6] In this study, we have successfully synthesized and characterized two novel Ru(II) complexes, which have 2,2'-bipyridyl (bpy) and a pincer-type tridentate ligand with two NHC moieties as the ancillary ligands. The pincer-type ligand coordinates to the Ru(II) center with the meridional manner. In the Ru(II) complexes, intramolecular CH/π interaction is formed between the *i*-Pr groups of the NHC moieties and the bpy ligand to fix the two NHC moieties in different circumstances each other.

Syntheses of [Ru^{II}(C^Py^C)(bpy)(MeCN)]$^{2+}$ (**1**) and [Ru^{II}Cl(C^Py^C)(bpy)]$^+$ (**2**) (C^Py^C = 2,6-bis(3-isopropyl-imidazol-2-ylidene)pyridine) are shown in Scheme 1 and the details are described in the Supporting Information (SI). Characterization of **1** and **2** was performed with ^{1}H NMR spectroscopy (Figure S1), ESI-TOF-MS spectrometry (Figure S2), elemental analysis and X-ray crystallography (Figure 1).

The crystal structures of **1**·(PF$_6$)$_2$ and **2**·PF$_6$ (Figure 1) clearly reveal that the coordination manner of the C^Py^C ligands is meridional. The bond distances of Ru1-N8(CH$_3$CN) in **1**·(PF$_6$)$_2$ and Ru1-Cl1 in **2** are 2.041(2) Å and 2.4348(6) Å, respectively. These values were within the range of the

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Supporting information for this article is given via a link at the end of the document.

Scheme 1. Synthesis of a Ru(C^Py^C)(bpy) complexes, **1** and **2**. dmso = dimethylsulfoxide.

corresponding bond lengths observed in other Ru(II) complexes having an acetonitrile molecule (2.03 – 2.44 Å)[7] or a chloride ion (2.39 – 2.52)[8] as a ligand. In addition, the bond lengths between the Ru(II) center and NHC-carbons (Ru1-C11 and Ru1-C1) in **1**·(PF$_6$)$_2$ are 2.093(2) and 2.097(2) Å, respectively, and those in **2**·PF$_6$ are 2.0824(19), 2.1149(19) Å, respectively. These values were longer than those of Ru-C bonds (1.98 – 2.00 Å) observed in other Ru(II)-NHC complexes.[3d, 9] This indicates the strong *trans* influences provided by strong σ-donating NHC ligands that are positioned mutually at the *trans* position.[10]

^{1}H NMR spectra of **1** and **2** in acetonitrile-*d*$_3$ exhibited complicated spectral patterns derived from the structures of **1** and **2** despite of meridional coordination geometry mentioned above. This indicates that complexes **1** and **2** show the *C*1 symmetry due to non-flexibility of the NHC ligand twisted at the CH$_2$-linkers. The ^{1}H NMR signals, assigned to the protons at the 6-position of the pyridine moieties in the bpy ligand close to the axial ligands, were observed in 9.3 for **1** and 10.0 ppm for **2**. The large down-field shift of the ^{1}H NMR signal in **2** compared to that of **1** indicates that there is hydrogen-bonding interaction between the proton at the 6-position of the bpy ligand and the Cl ligand in **2** (Figure S3(a) in SI).[3d] ^{1}H NMR signals of the methylene moieties showing two AB quartets were observed in the range from 4.8 to 5.6 ppm for **1**. These chemical shifts were comparable to those of Ru(II) complexes having two similar bis-NHC ligands.[11] The ^{1}H NMR spectrum of **2** showed an AB quartet and two AX doublets in the range from 4.9 to 7.0 ppm for the methylene moieties. The large downfield shift of one of the AX doublets for **2** due to the methylene protons should be derived from intramolecular hydrogen bonding between the chloro ligand and one methylene proton as shown in Figure S3 (SI). Three possible structural isomers can be considered for **1** and **2**: one meridional and two facial isomers (Figure S4). Since **1** and **2** should be in the *C*1 symmetry as indicated by the ^{1}H
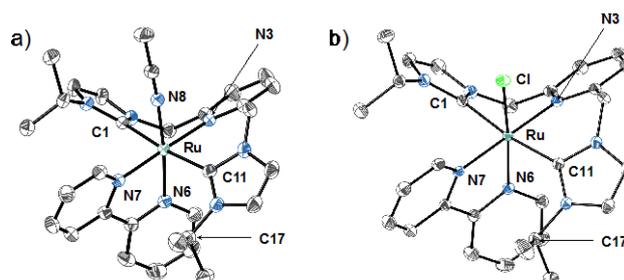
Figure 1. ORTEP drawings of **1** (a) and **2** (b) with 50% probability of thermal ellipsoids. The counter anions and hydrogen atoms are omitted for clarity.

NMR spectra, one of the facial isomers in the *Cs* symmetry can be excluded. In addition, the hydrogen bonding between the chloro ligand and the proton at the 6-position of the bpy ligand in **2**, as mentioned above, should not be observed in the other facial isomer. The features observed in the ^{1}H NMR spectra indicate that the C^Py^C coordinates to the Ru(II) center in the meridional manner in both **1** and **2**, as demonstrated by X-ray crystallography.

In the crystal structures, the bpy ligand in both **1** and **2** was strongly distorted due to the steric repulsion of one of the isopropyl moieties bound to the NHC ligand (Figure S3(b) and (c)). The distance between C17 and the centroid of the pyridine ring containing N7 atom was *ca.* 3.7 Å, which was in the range (2.9 – 3.8 Å) that CH/π interaction can be formed between them.[12] This interaction suggests shielding of the proton by the ring current to afford large upfield shifts (> 2 ppm) of the ^{1}H NMR signals, assigned to protons bound to the methine carbons (Figures S5 and S6).[13] In addition, variable-temperature ^{1}H NMR measurements from 298 to 348 K were conducted for **1**; as a result, the ^{1}H NMR signals did not show any significant shifts and the symmetry-broken ^{1}H NMR signals of **1** maintained in the temperature range (Figure S10). This indicates that the CH/π interaction assists the stabilization of the distorted conformation of the C^Py^C ligand in **1** and the two NHC moieties do not flip to show the seesaw-like motion that makes the two NHC moieties equivalent in the NMR time scale.[14]

In the UV-Vis spectra of **1** and **2** in acetonitrile, characteristic absorption bands were observed at 483 and 537 nm, respectively. On the basis of the TD-DFT calculations

(Figure S11), these absorption bands are assigned to metal-to-ligand charge transfer (MLCT) bands ($d\pi$ of Ru(II) to π^* of bpy). These wavelength values were larger (*ca.* 30 nm) compared to other related Ru(II) complexes having bpy ligands.[15] In addition, the emission and excitation spectra of **1** and **2** were measured in argon-purged butyronitrile at 77 K (Figure 2b and c). The emission bands assigned to the phosphorescence from the [3]MLCT excited states of **1** and **2** were observed at 608 and 732 nm, respectively.[16] The quantum yields of **1** and **2** were determined to be 0.41 and 1.5 × 10^{-3}, respectively.[17 – 19] This lowering of the quantum yield for the phosphorescence in **2** can be explained by decreasing the lifetime of the [3]MLCT excited state by thermal transition to metal-centered triplet excited state ([3]MC); this is probably due to the narrowing the ligand field splitting in **2**, since the chloro ligand acts as a π-donor to elevate the energy level of the $d\pi$ orbital in contrast to the acetonitrile ligand in **1**, which undergoes π-back bonding to lower that of the $d\pi$ orbital and to enlarge the splitting. As the result, thermal transition from the [3]MLCT excited state to the [3]MC excited state occurs easily in **2**. The effects of axial ligands on the photophysical properties of the Ru(II) complexes have been also reported for Ru(II)-porphyrin complexes.[20]

The redox behavior of **1**·(PF$_6$)$_2$ and **2**·PF$_6$ in the acetonitrile solutions was investigated by cyclic and differential-pulse voltammetries at room temperature (Figure S13). The cyclic voltammograms (CVs) showed reversible redox waves at $E_{1/2}$ = +1.01 and −1.49 V vs SCE for **1**·(PF$_6$)$_2$ and $E_{1/2}$ = +0.62 and −1.52 V vs SCE for **2**·(PF$_6$). These potentials were relatively lower than those of other related Ru(II) complexes having neutral polypyridyl ligands or alkylamine ligands.[21] In particular, redox potentials of **1** and **2** were lower than Ru(II) complexes having terpyridine-like conjugated NHC ligands.[6] This indicates that the σ-donating ability of the NHC moieties in C^Py^C ligand is stronger than the π-conjugated analog,[6] and the strong σ-donating ability of the NHC ligands in the C^Py^C ligand makes the Ru(II) center more electron-rich. Therefore, the Ru(II) center can be oxidized more easily than the π-conjugated counterparts.[6]
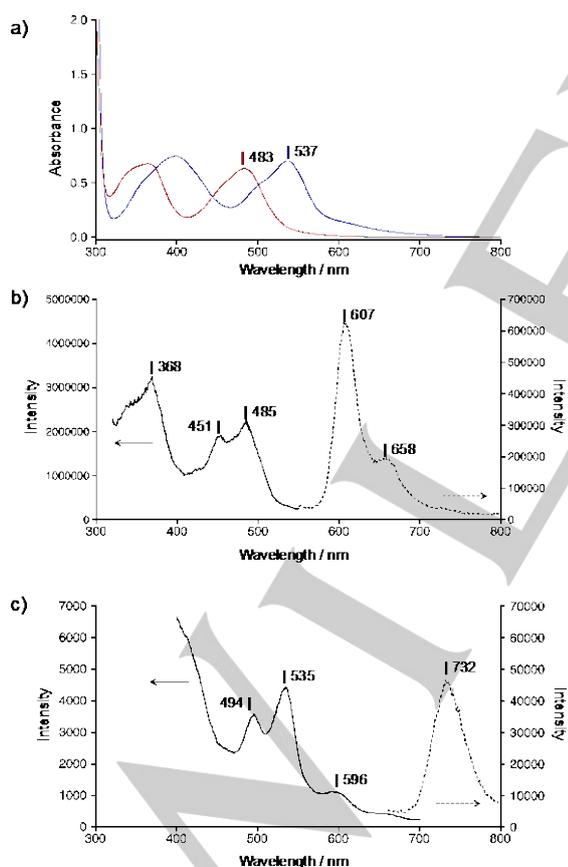

Figure 2. a) UV-Vis spectra of **1** (red) and **2** (blue) in MeCN measured at room temperature. b) Excitation (solid line) and emission spectra (dashed line) of **1** in butyronitrile glass measured at 77 K under Ar: [**1**] = 0.1 mM, λ_{exc} = 486 nm, λ_{obs} for the excitation spectrum = 608 nm. c) Excitation (solid line) and emission spectra (dashed line) of **2** in butyronitrile measured at 77 K under Ar: [**2**] = 0.1 mM, λ_{exc} = 544 nm, λ_{obs} for the excitation spectrum = 732 nm.
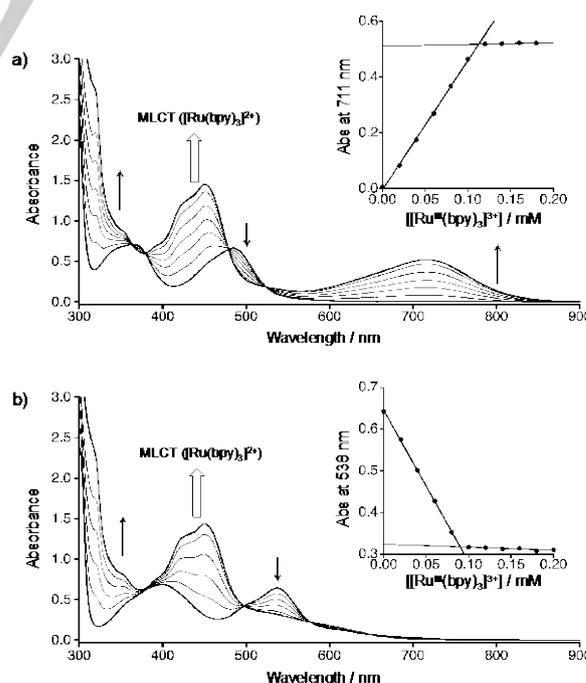

Figure 3. UV-Vis spectral changes upon addition of [Ru^{III}(bpy)$_3$]$^{3+}$ to **1** (a) and **2** (b) at room temperature. [**1**] and [**2**]: 0.10 mM. Solvent: MeCN. Inset shows the absorbance change at the selected wavelength against concentration of [Ru^{III}(bpy)$_3$]$^{3+}$ added as an oxidant.

Upon addition of $[Ru^{III}(bpy)_3](ClO_4)_3$ ($E_{1/2}$ = +1.29 V vs SCE)[22] to acetonitrile solutions of **1** and **2**, the absorption bands at 483 nm for **1** and 537 nm for **2** decreased and instead a new obvious absorption bands at 711 nm for **1** and 600 nm for **2** arose with an isosbestic point at 363 and 478 nm for **1** and 497 and 577 nm for **2** (Figures 3). The absorption increase around 450 nm was derived from the formation of $[Ru^{II}(bpy)_3]^{2+}$, which matched to the absorption band of $[Ru^{II}(bpy)_3](PF_6)_2$ (Figure S14). The changes were completed by addition of 1 equiv of $[Ru^{III}(bpy)_3](ClO_4)_3$; the solution color changed from orange to green for **1** in the formation of the 1e$^-$-oxidized species (**3**) and from pink to red for **2** in that of the 1e$^-$-oxidized species (**4**). Based on the TD-DFT calculations, the absorption band of 1e$^-$-oxidized **1** at 711 nm was assigned to the ligand-to-metal charge transfer (LMCT) transition from the NHC ligand, having an *iso*-propyl group forming the CH/π interaction with the pyridine ring containing N7 atom, to the Ru(III) center in **3** (Figure S15). The ^{1}H NMR spectra of **3** and **4** showed relatively broad signals in the range of −74 ~ +60 ppm and −40 ~ +20 ppm, respectively, reflecting the paramagnetic characters of **3** and **4** (Figure S16 and S17).[23] The electron paramagnetic resonance (EPR) spectra recorded in acetonitrile at 5 K exhibited rhombic EPR signals[24] with g_1 = 2.782, g_2 = 2.315 and g_3 = 1.980 for **3**, and g_1 = 2.984, g_2 = 2.116 and g_3 = 1.758 for **4** (Figure 4). The root mean squares of the g-values, <g> (= $((|g_1|^2 + |g_2|^2 + |g_3|^2)/3)^{1/2}$), were calculated to be 2.382 and 2.343, respectively, which were comparable to a typical <g> value for Ru(III) complexes (S = 1/2), *ca.* 2.3.[25] Thus, the products of the first oxidation processes of **1** and **2** should be formally $[Ru^{III}(C{\wedge}Py{\wedge}C)(bpy)(NCMe)]^{3+}$ (**3**) and $[Ru^{III}Cl(C{\wedge}Py{\wedge}C)(bpy)]^{2+}$ (**4**), respectively.

DFT-optimized structures of complexes **1** and **2** under vacuum were calculated and shown in Figure 5. The highest occupied molecular orbital (HOMO) of **1** mainly delocalized on the Ru(II) center and also on the NHC ring forming CH/π interaction with the pyridine ring. In contrast, that of **2** delocalized on the Ru(II) center, Cl ligand and NHC rings. The lowest unoccupied molecular orbital (LUMO) of both of **1** and **2** located on the bpy ligands. These results indicate that the first oxidation of **1** and **2** should occur on the Ru(II) center and the first reduction of them should proceed on the bpy ligand. In addition, the spin-density maps of **3** and **4** were obtained based on their DFT-optimized structures, and the unpaired electrons mainly located on the Ru center and NHC moiety in both **3** and **4**. The spin density on the Ru center was calculated to be 0.88 for
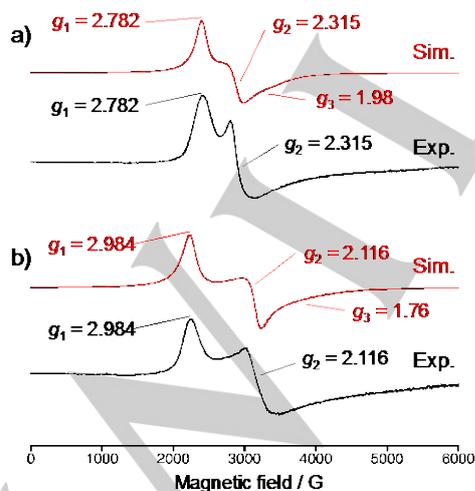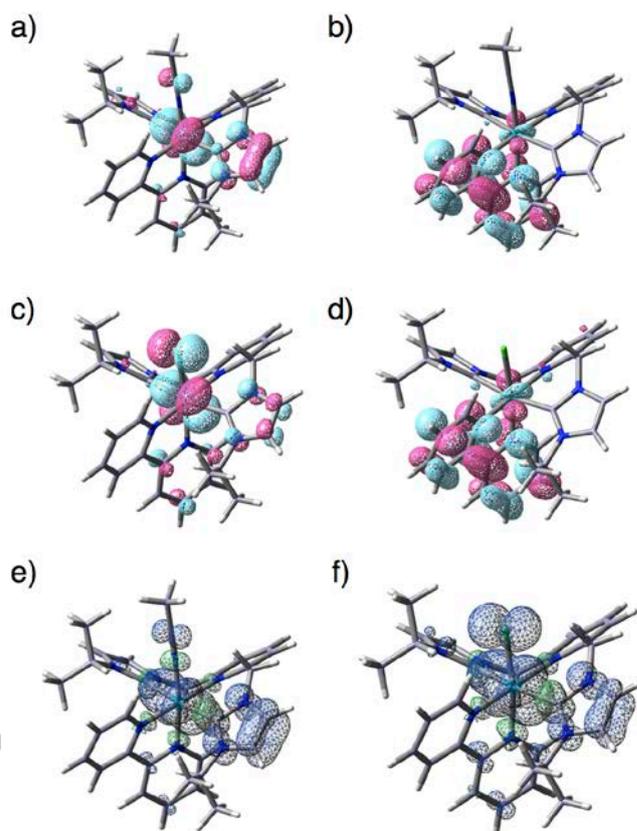

Figure 5. HOMO (a) and LUMO (b) orbitals of **1**, HOMO (c) and LUMO (d) orbitals of **2**, and Mulliken spin-density map (blue and green mesh) of **3** (e) and **4** (f) calculated at the UB3LYP/SDD level of theory.

3 and 0.86 for **4**. Therefore, almost of all unpaired electron localized on the Ru center, allowing us to conclude that the first oxidation should occur at the Ru center to afford formally Ru(III) complexes. These results are consistent with the results of EPR measurements (Figure 4).

In conclusion, novel two Ru(II) complexes having pincer-type C^Py^C ligands have been successfully synthesized and characterized on the basis of crystallographic and spectroscopic analyses. The methylene-bridged NHC ligand (C^Py^C) coordinated in a meridional manner and highly distorted, which was maintained even in solution, where the intramolecular CH/π interaction between the *i*Pr group of the NHC moieties and the bpy ligand probably assists the fixation of the distorted structure of the C^Py^C ligand. NHC ligands had a strong σ-donating ability to Ru(II) centers compared to pyridine or alkylamine ligands, resulted in lowering oxidation potential of the Ru(II)/Ru(III) redox couple. In addition, these two Ru(II) complexes could be oxidized by using 1e$^-$-oxidant in acetonitrile to afford the corresponding Ru(III) complexes, which were revealed by ^{1}H NMR and EPR spectroscopic analyses and DFT calculations. The applications of these complexes in catalysis and optical functionality are ongoing in our laboratory.

Figure 4. Experimental EPR spectra (black) and their simulations (red) for 1e$^-$-oxidized species of **1** (a) and **2** (b) measured at 5 K in helium-purged MeCN. [**1**] or [**2**] = 1 mM, MW power: 5.024 mW, MW frequency: 9.398 GHz, Mod. frequency: 100.00 kHz, Mod. amplitude: 12.00 G. 1 equiv. of $[Ru^{III}(bpy)_3](ClO_4)_3$ was used for 1e$^-$ oxidation.

Acknowledgements

[1] a) D. Pugh, A. A. Danopoulos, *Coord. Chem. Rev.* **2007**, *251*, 610-641; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172; c) H. D. Velazquez, F. Verpoort, *Chem. Soc. Rev.* **2012**, *41*, 7032-7060.

[2] S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676.

[3] a) M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree, E. Peris, *Organometallics* **2003**, *22*, 1110-1114; b) M. Dakkach, X. Fontrodona, T. Parella, A. Atlamsani, I. Romero, M. Rodríguez, *Adv. Synth. Catal.* **2011**, *353*, 231-238; c) L. Vaquer, P. Miró, X. Sala, F. Bozoglian, E. Masllorens, J. Benet-Buchholz, X. Fontrodona, T. Parella, I. Romero, A. Roglans, M. Rodríguez, C. Bo, A. Llobet, *ChemPlusChem* **2013**, *78*, 235-243; d) Y. Shimoyama, T. Ishizuka, H. Kotani, Y. Shiota, K. Yoshizawa, K. Mieda, T. Ogura, T. Okajima, S. Nozawa, T. Kojima, *Angew. Chem. Int. Ed.* **2016**, *55*, 14041-14045.

[4] a) R. Staehle, L. Tong, L. Wang, L. Duan, A. Fischer, M. S. G. Ahlquist, L. Sun, S. Rau, *Inorg. Chem.* **2014**, *53*, 1307-1319; b) H.-J. Liu, M. Gil-Sepulcre, L. Francás, P. Nolis, T. Parella, J. Benet-Buchholz, X. Fontrodona, J. García-Antón, N. Romero, A. Llobet, L. Escriche, R. Bofill, X. Sala, *Dalton Trans.* **2017**, *46*, 2829-2843.

[5] a) G. J. Barbante, P. S. Francis, C. F. Hogan, P. R. Kheradmand, D. J. D. Wilson, P. J. Barnard, *Inorg. Chem.* **2013**, *52*, 7448-7459; b) S. U. Son, K. H. Park, Y.-S. Lee, B. Y. Kim, C. H. Choi, M. S. Lah, Y. H. Jang, D.-J. Jang, Y. K. Chung, *Inorg. Chem.* **2004**, *43*, 6896-6898.

[6] L.-H. Chung, K.-S. Cho, J. England, S.-C. Chan, K. Wieghardt, C.-Y. Wong, *Inorg. Chem.* **2013**, *52*, 9885-9896.

[7] a) S. C. Rasmussen, S. E. Ronco, D. A. Mlsna, M. A. Billadeau, W. T. Pennington, J. W. Kolis, J. D. Petersen, *Inorg. Chem.* **1995**, *34*, 821-829; b) T. Kojima, K. Nakayama, M. Sakaguchi, T. Ogura, K. Ohkubo, S. Fukuzumi, *J. Am. Chem. Soc.* **2011**, *133*, 17901-17911; c) K. Arora, J. White, R. Shama, S. Mazumder, P. Martin, H. B. Schlegel, C. Turro, J. J. Kodanko, *Inorg. Chem.* **2016**, *55*, 6968-6979.

[8] a) H.-W. Tseng, R. Zong, J. T. Muckerman, R. Thummel, *Inorg. Chem.* **2008**, *47*, 11763-11773; b) S. Ohzu, T. Ishizuka, H. Kotani, T. Kojima, *Chem. Commun.* **2014**, *50*, 15018-15021; c) T. Kojima, T. Morimoto, T. Sakamoto, S. Miyazaki, S. Fukuzumi, *Chem. Eur. J.* **2008**, *14*, 8904-8915; d) H. Mitome, T. Ishizuka, H. Kotani, Y. Shiota, K. Yoshizawa, T. Kojima, *J. Am. Chem. Soc.* **2016**, *138*, 9508-9520.

[9] M. Dakkach, A. Atlamsani, T. Parella, X. Fontrodona, I. Romero, M. Rodríguez, *Inorg. Chem.* **2013**, *52*, 5077-5087.

[10] The strain of the six-membered chelate rings might cause the elongation of the Ru-C coordination bonds; however, in Ru(II) complexes, having a methylene-bridged NCN-type ligand and showing similar structural distortion as observed in **1** and **2** due to formation of the six-membered chelate rings, the Ru-N bond lengths were in the typical range of those for Ru(II)-polypyridyl complexes (see: D. E. Prokopchuk, B. T. H. Tsui, A. J. Lough, R. H. Morris, *Chem. Eur. J.* **2014**, *20*, 16960-16968). Therefore, the elongation of the Ru-C bonds in **1** and **2** are probably derived from the mutual *trans*-influence.

[11] J. Dinda, S. Liatard, J. Chauvin, D. Jouvenot, F. Loiseau, *Dalton Trans.* **2011**, *40*, 3683-3688.

[12] a) H. Suezawa, S. Ishihara, Y. Umezawa, S. Tsubonoya, M. Nishio, *Eur. J. Org. Chem.* **2004**, 4816-4822; b) O. Sénèque, M. Giorgi, O. Reinaud, *Chem. Commun.* **2001**, 984-985.

[13] We also investigated nuclear Overhauser effect (NOE) of **1** in acetonitrile-d_3 to assign the desymmetrized ^{1}H NMR signals. See Figure S7 ~ S9 in the SI.

[14] The steric strain around the CH$_2$ moieties of the C^Py^C ligand may contribute to the stabilization of the geometry in **1**. However, Suárez and coworkers reported that Ru(II) complexes, having a CNC-type bis-NHC ligand with the meridional conformation, exhibited the seesaw-like motion to exchange the positions of the left and right NHC moieties above and below the equatorial plane even at RT (See: M. Hernández-Juárez, J. López-Serrano, P. Lara, J. P. Morales-Cerón, M. Vaquero, E. Álvarez, V. Salazar, A. Suárez, *Chem. Eur. J.* **2015**, *21*, 7540-7555.) This kind of motions was not observed for **1** in the temperature range of 298 – 348 K in acetonitrile-d_3. Therefore, the strain of the CH$_2$ bridges forming six-membered chelate rings cannot explain the stabilization of the geometry for **1**. We think that the CH/π interaction between the methine CH of the *i*Pr groups and the bpy ligand plays an important role for the stabilization of the geometry.

[15] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. V. Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85-277.

[16] Phosphorescence derived from the ^{3}MLCT excited state of **1** was partially quenched in an O$_2$-saturated butyronitrile solution measured at room temperature. See Figure S12 in the SI.

[17] The quantum yields of phosphorescence of **1** and **2** were determined by comparison with the reported quantum yield (ϕ_{em} = 0.35) of [Ru(bpy)$_3$]$^{2+}$ in MeOH : EtOH = 1 : 4 (v/v) glass at 77 K. G. A. Crosby, W. H. Elfring, Jr., *J. Phys. Chem.* **1976**, *80*, 2206-2211.

[18] To compare the quantum yields with other Ru(II)-polypyridyl complexes, emission spectral analyses were also conducted at room temperature (see Table S1 in the SI and ref. 19). As a result, the phosphorescence quantum yields of **1** and **2** were determined to be 7.0×10^{-4} and < 0.0001, respectively. These values fall in the range of those reported for other Ru(II) complexes: *i.e.* 0.062 for [Ru(bpy)$_3$]$^{2+}$,[19a] 5×10^{-6} for [Ru(tpy)$_2$]$^{2+}$ (tpy = 2,2';6',6"-terpyridyl),[19b] and 4.5×10^{-4} for [Ru(tpy)(bpy)(NCMe)]$^{2+}$.[19c]

[19] a) J. V. Casper, T. J. Meyer, *J. Am. Chem. Soc.* **1983**, *105*, 5583-5590; b) M. Maestri, N. Armaroni, V. Balzani, E. C. Constable, A. M. W. Cargill Thompson, *Inorg. Chem.* **1995**, *34*, 2759-2767; c) T. Moriuchi, J. Shiori, T. Hirao, *Tetrahedron Lett.* **2007**, *48*, 5970-5972.

[20] L. M. A. Levine, D. Holten, *J. Phys. Chem.* **1988**, *92*, 714-720.

[21] a) C.-N. Tsai, M. M. Allard, R. L. Lord, D.-W. Luo, Y.-J. Chen, H. B. Schlegel, J. F. Endicott, *Inorg. Chem.* **2011**, *50*, 11965-11977; b) L. Vaquer, A. Poater, J. D. Tovar, J. García-Antón, M. Solà, A. Llobet, X. Sala, *Inorg. Chem.* **2013**, *52*, 4985-4992.

[22] J.-C. Chambron, J.-P. Sauvage, E. Amouyal, P. Koffi, *Nouv. J. Chim.* **1985**, *9*, 527-529.

[23] Paramagnetic ^{1}H NMR spectra of Ru(III)-NHC complexes are relatively rare. A few examples of ^{1}H NMR spectra of Ru(III) complexes having polypyridyl ligands are shown below: a) T. Kojima, K. Hayashi, S. Iizuka, F, Tani, Y. Naruta, M. Kawano, Y. Ohashi, Y. Hirai, K. Ohkubo, Y. Matsuda, S. Fukuzumi, *Chem. Eur. J.* **2007**, *13*, 8212-8222; b) J. C. Dobson, B. P. Sullivan, P. Doppelt, T. J. Meyer, *Inorg. Chem.* **1988**, *27*, 3863-3866.

[24] The rhombic *g* values ($g_1 – g_3$) for **3** and **4** were determined with the ESR simulation. In the ESR spectra of **3** and **4**, there are no obvious peaks derived from g_3; however, the spectra could not be well reproduced with $g_\parallel$ and $g_\perp$ as the axial ESR signals.

[25] a) K. Matsuura, L. Kevan, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1763-1768; b) Y. Pushkar, D. Moonshiram, V. Purohit, L. Yan, I. Alperovich, *J. Am. Chem. Soc.* **2014**, *136*, 11938-11945; c) N. Gauthier, N. Tchouar, F. Justaud, G. Argouarch, M. P. Cifuentes, L. Toupet, D. Touchard, J.-F. Halet, S. Rigaut, M. G. Humphrey, K. Costuas, F. Paul, *Organometallics* **2009**, *28*, 2253-2266.
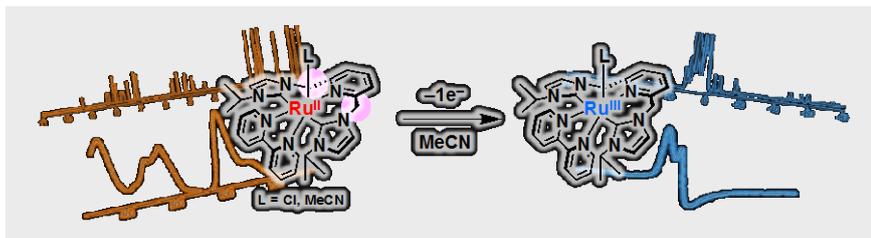
Two Ru(II) complexes, having an axial ligand, bipyridine and a pincer-type methylene-bridged *N*-heterocyclic carbene ligand, have been synthesized. Their structural, electrochemical, and photochemical properties have been investigated, which revealed the characteristics of a methylene-bridged pincer-type NHC ligand.

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Ruthenium(II) Complexes Having a Pincer-Type Ligand with Two *N*-Heterocyclic Carbene Moieties