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Toward a Photochemical and Thermal Molecular Machine: Reversible Ligand Dissociation and Binding in a Ruthenium(II)-2,2′-bipyridine Complex with Tris(2-pyridylmethyl)amine

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A Ru^{II} complex having tris(2-pyridylmethl)amine (TPA) and 2,2′-bipyridine (bpy), [Ru(TPA)(bpy)]X_2 (X = ClO_4, PF_6), exhibited a severe distortion of the coordination of the axial pyridine moiety of TPA due to steric hindrance. The complex showed interesting dissociation-binding behavior of the axial pyridine arm to form a solvent adduct with TPA ligation in a unique meridional tridentate fashion. The complex undergoes thermal dissociation to form solvent-coordinated species via an S_N2-like mechanism with activation energy of 117 kJ/mol. In contrast, the complex showed reversible photochemical dissociation and rebinding via an S_N1-like mechanism by MLCT irradiation. The photochemical dissociation was accelerated ~200-fold faster than the thermal process. The dissociation process involves selective binding behavior toward external ligands (solvents) with π-acceptor character, which is indispensable, and no σ-donating molecules could bind to the Ru^{II} center. The guest molecule can be released upon photoirradiation after its thermal binding.

Recent advances on molecular machines have attracted much attention due to their potential, for example, to transfer signals, transduce information, and perform functions by virtue of mechanical motions at the molecular level.[1] Regulation of the molecular motion by external stimuli such as light, redox, or heat is essential for such molecular machinery. In addition, these molecules should have a stationary part and a mobile part,[2] and those two components need to cooperate to achieve the desired functionality in a mechanical manner. Molecular machines reported so far are acting in, for example, translocation of metal ions,[3] shuttlelike

behavior in rotaxane scaffolds[4] by redox, photoirradiation, and pH change as driving forces. Although interesting molecular motions have been reported, the functions of such molecular machines are poorly established, and the utilization and application of such mechanical motions need to be explored. On the other hand, molecular motion in the coordination sphere of transition metal complexes has been observed, such as ligand dissociation and rebinding to exhibit chemical function,[5] and activation of external substrates at a vacant site formed in enzymatic catalysis as observed for copper-containing amine oxidases.[6] Thus, mechanical motions in coordination spheres play an indispensable role in the chemical and biological processes.

Tris(2-pyridylmethyl)amine (TPA) usually acts as a tripodal tetradentate ligand that forms stable complexes with various metal ions. In some cases, the TPA ligand can also coordinate to the metal center in a tridentate fashion and have an uncoordinating pyridine arm.[7] In such tridentate situations, TPA binds in a facial configuration in an octahedral environment. In this paper, we describe novel photochemical and thermal behavior of the TPA ligand bound to a Ru^{II}-bpy fragment. The complex induces a novel meridional coordination of the tridentate TPA and molecular recognition behavior toward π-acceptor ligands at the Ru^{II} center. The reaction of bpy with a bis-μ-chloro dimer [RuCl(TPA)]$_2$(ClO_4)$_2$[8] in methanol provides a reasonable synthetic route to access to a novel Ru^{II}-bpy complex with TPA, [Ru(TPA)(bpy)](ClO_4)$_2$ (**1**), in good yields. The reaction of bpy

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(8) Kojima, T.; Amano, T.; Ishii, Y.; Ohba, M.; Okaue, Y.; Matsuda, Y. *Inorg. Chem.* **1998**, *37*, 4076–4085. **Safety note:** Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled with great care in small quantities.
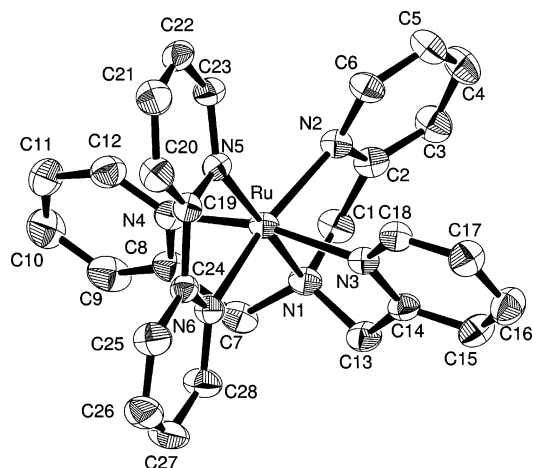
Figure 1. An ORTEP drawing of the cation moiety of **1** with numbering scheme (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−N1 2.085(3), Ru−N2 2.102(3), Ru−N3 2.048(3), Ru−N4 2.078(3), Ru−N5 2.065(3), Ru−N6 2.101(3); N1−Ru−N2 79.1(1), N1−Ru−N3 83.5(1), N1−Ru−N4 80.6(1), N2−Ru−N3 80.7(1), N2−Ru−N4 101.9(1), N5−Ru−N6 77.3-(1).

with [Ru^{III}Cl$_2$(TPA)]ClO$_4$ in EtOH/H$_2$O (1:1 v/v) at reflux also gave **1** in a comparable yield.

In the crystal structure of **1** (Figure 1),[9] elongated bond lengths were observed for Ru−N2 (2.102(3) Å) and Ru−N6 (2.101(3) Å), which consist of an axial pyridine moiety of the TPA ligand and one pyridine ring of bpy, respectively. The interatomic distance between C6 of the axial pyridine of TPA and C23 of the 6-position of the equatorial pyridine of bpy was 3.285(6) Å, and that of the hydrogens attached to the corresponding carbon was also short to be 2.129 Å. This close contact was clearly shown in the differential ^{1}H NOE NMR spectrum of **1** in CD$_3$CN (Figure S2), indicating that the steric congestion is not relaxed even in solution. This steric congestion is thought to be a driving force for the dissociation of the axial pyridine arm of the TPA ligand, as described below.

The UV−vis spectrum of **1** in CH$_3$CN showed absorption maxima at 247, 293, 371, 423, and 453 nm (Figure S6). Assignments for these absorption bands were made on the basis of reported assignments for similar complexes.[7] The absorption at 245 nm was assigned to $\pi-\pi^*$ transition of TPA pyridines and that at 289 nm was due to $\pi-\pi^*$ transition of bpy ligand. The peak due to MLCT from ruthenium to the TPA ligand was observed at 371 nm, and those at 423 and 453 nm were assigned to MLCT from ruthenium to the bpy ligand.

During NMR measurements of **1** in CD$_3$CN, we observed new peaks at 3.21 ppm (singlet) and 4.14 and 4.64 ppm (AB quartet, J_{AB} = 17 Hz) and other peaks in the aromatic region as shown in Figure 2. The ESI-MS spectrum of a mixture showed a new cluster of peaks at 736.9, which suggests that the new species is {[Ru(TPA)(bpy)(CD$_3$CN)](PF$_6$)}$^+$ ({**2**·
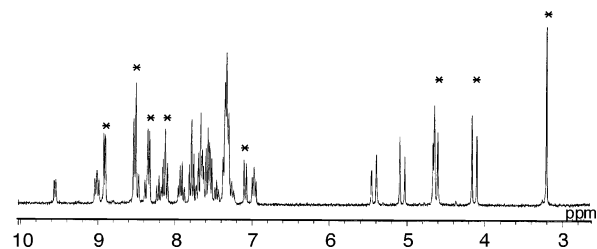
Figure 2. ^{1}H NMR spectrum of the reaction mixture of **1** and **2** (asterisks) in CD$_3$CN.

Scheme 1. Interconversion between **1** and **2**
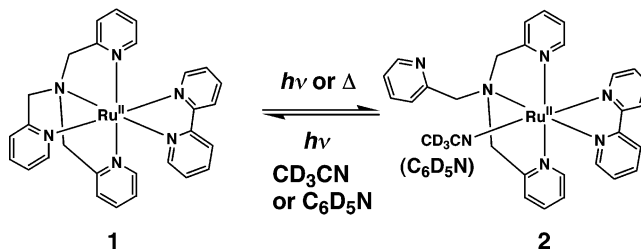
PF$_6$}$^+$; Figure S3).[10] On the basis of the NMR spectrum, complex **2** possesses a TPA ligand in a unique meridional tridentate fashion. We followed this reaction by NMR spectroscopy and determined the apparent first-order rate constant of the reaction to be 1.73 × 10^{-7} s^{-1} at room temperature under air. Upon irradiation of the sample at the MLCT region by a 500 W Xe arc lamp (l = 20 cm) with IR- and UV-cutoff filters[11] under aerobic conditions, however, we observed drastic acceleration of the reaction at room temperature, approximately 200-fold faster than that without MLCT-irradiation. These data clearly show that the reaction is accelerated by photoirradiation and that the MLCT excitation is responsible for the reaction. In addition, the reverse reaction was observed after 17 h irradiation. The reverse reaction was apparently 14-fold slower than the forward reaction. This reverse reaction was also photoinductive, probably due to MLCT excitation to release the coordinated CD$_3$CN in **2**. We propose that this reaction is a reversible dissociation/recoordination of the axial pyridine arm of the TPA ligand to form an uncoordinated pyridine arm as shown in Scheme 1. As described in the scheme, the thermal one-way dissociation was also observed as mentioned below. This reaction proceeded also in pyridine-d_5 without photoirradiation at room temperature at a similar rate (1.54 × 10^{-7} s^{-1}) to give [Ru(TPA)(bpy)(C$_5$D$_5$N)]$^{2+}$ (m/z = 777.0 (ESI-MS); {[Ru(TPA)(bpy)(C$_5$D$_5$N)](PF$_6$)}$^+$, Figure S4).

[Ru(bpy)$_3$]X$_2$ has been known to undergo photoinduced substitution reactions upon MLCT excitation via ^{3}MC that is coupled with ^{3}MLCT through spin−orbit coupling to form a five-coordinate intermediate.[12] Recently, Sauvage and co-workers have reported that photochemical ligand dissociation and thermal recoordination can be observed in a Ru(1,10-

(9) In the course of this project, Wolny and co-workers have reported the crystal structure of **1** independently: Bjernemose, J.; Hazell, A.; McKenzie, C. J.; Mahon, M. F.; Nielsen, L. P.; Rainthby, P. R.; Simonsen, O.; Toftlund, H.; Wolny, J. A. *Polyhedron* **2003**, *22*, 875−885.

(10) [Ru(TPA)(bpy)(CH$_3$CN)](PF$_6$)$_2$ was prepared by the reaction in CH$_3$-CN. ^{1}H NMR (270 MHz, CD$_3$OD): δ = 2.45 (s, 3H, CH$_3$). IR (KBr): 2266 cm^{-1} (ν(C≡N)). These data indicate that the nitrile ligand coordinates to the ruthenium center in an η^1-N fashion.

(11) IR-cut filter (IRA-20; Toshiba Glass) and UV-cut filter (UV-D33S; Toshiba Glass) were used.

(12) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803−4810.

phenanthroline)$_2$L complex[13] and a Ru(II) complex with a scorpionate terpyridine complex.[14] In their systems, the molecules undergo photochemical ligand dissociation and thermal and/or photochemical rebound of bpy ligands. These observations are opposite to our results presented in Scheme 1.

The thermal reaction was examined by incubating an NMR sample of **1** in CD$_3$CN at 50 °C in the dark. In this case, the amount of **2** increased monotonically with a first-order rate constant of 1.50×10^{-5} s^{-1}; however, the reaction rate was slower than that with MLCT irradiation. In this case, the ratio of [**2**]/[**1**] went up to >30 ($K = 32.6$ at 50 °C), almost quantitative conversion. An Arrhenius plot (Figure S5) allowed us to estimate the activation energy of the thermal ligand dissociation in CD$_3$CN to be 117 kJ/mol (28.2 kcal/mol). This clearly shows that the ligand dissociation of the axial pyridine of TPA should proceed thermodynamically, and the back reaction, i.e., the recoordination of the axial pyridine of TPA, should be accompanied by a photoinduced solvent dissociation.[15] This argument is supported by the observation of recovery of **1** by photoirradiation of **2**, which is formed by refluxing **1** in CH$_3$CN in the dark.

We also examined other solvents such as CD$_2$Cl$_2$, D$_2$O, CD$_3$OD, and DMSO-d_6; however, no reaction was observed at room or elevated temperatures without irradiation. These observations suggest that the reaction requires coordinatable solvents with a π-conjugation system (π-acceptor character) for π-back-bonding and less steric hindrance to bind the ruthenium center. With DMSO, however, photoirradiation gave two kinds of products, which contained DMSO as ligands, and those formations were not straightforward.[16] Those observations suggest that the transition states are different for thermal and photochemical processes. We assume that an S$_N$1-like transition state is produced in the photoinduced reaction, in contrast to an S$_N$2-like transition state for the thermal reaction, as summarized in Scheme 2. Therefore, the more sterically bulky DMSO does not bind to the ruthenium center in the thermal process. The steric effects arise from the close proximity of the two pyridine rings as described above, and the steric effects can discriminate the external molecules to bind the metal center. Thus, in addition to the electronic requirements, the steric effects could give molecular recognition ability to **1**. Along the

Scheme 2. Proposed Mechanism of Mechanical Motion of **1**
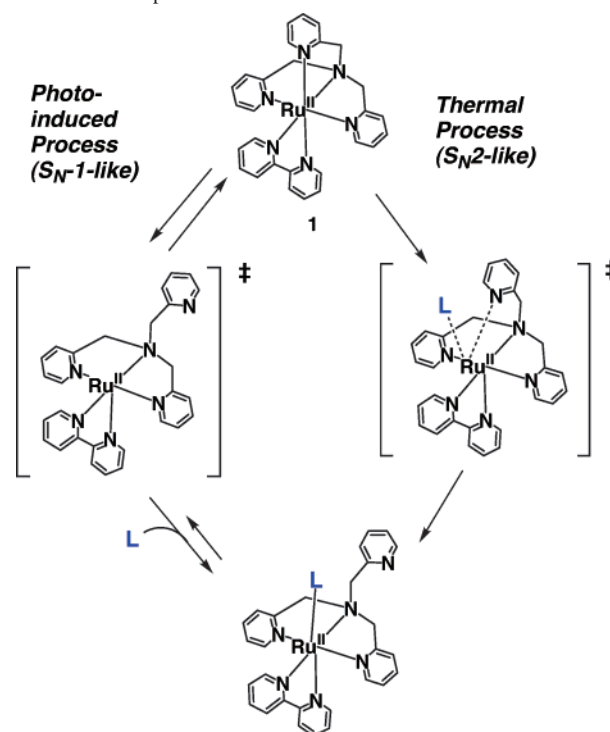
L; π-acceptor-character is required

clockwise mechanism in Scheme 2, the binding and releasing of the recognized guest molecule can be achieved by different driving forces, even if the releasing process is 40% effective.

In summary, a novel Ru-bpy complex with the tripodal TPA ligand showed a unique reversible photochemical and thermal ligand dissociation of TPA. The driving force is steric hindrance between the bpy and TPA and the intrinsically weakened coordination of the axial pyridine of TPA due to sharing π-back-bonding with bpy. Compound **1** described here could be a new photo- and thermoswitchable molecule having a potentially vacant site to perform selective complexation with π-acceptors. In addition, this system presented here can be expected to apply to chemical reactions and to construct switchable supramolecular assemblies, as a novel molecular machine.

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(15) Hecker, C. R.; Fanwick, P. E.; McMillin, D. R. *Inorg. Chem.* **1991**, *30*, 659−666.
(16) In DMSO-d_6 upon irradiation, we observed complicated reaction processes, probably involving photoisomerization of bound DMSO molecule. See: Alessio, E.; Mestroni, G.; Nardin, G.; Attia, W. M.; Calligaris, M.; Sava, G.; Zorzet, S. *Inorg. Chem.* **1988**, *27*, 4099−4106.