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Photoswitchable Molecular Lock. One-Way Catenation of a Pt(II)-Linked Coordination Ring via the Photolabilization of a Pt(II)−Pyridine Bond

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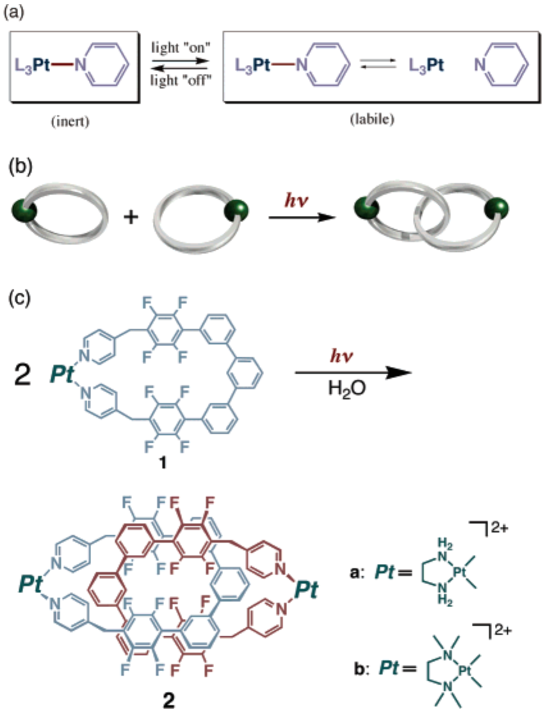
An inert coordination bond that becomes labile under external stimuli can be termed "molecular lock" because a closed (locked) structure incorporating an inert bond is equilibrated with an open (unlocked) structure via the labilization of the inert bond. A Pt(II)−py bond (py = pyridyl group) has been previously described as a thermally switchable molecular lock because its inert nature becomes labile at high temperature in the presence of a salt.[1] However, the salt-assisted thermal switching (locking/unlocking) is not a clean and facile process because of salt contamination and tedious procedures in salt removal. Here we report a precise, clean molecular lock that operates by light. We have found that the inert Pt(II)−py bond, whose photochemistry has attracted little attention, is considerably labilized upon UV irradiation (Scheme 1a). We demonstrate the photoswitchable molecular lock by the one-way catenation of coordination rings.[2,3] Namely, Pt(II)-linked ring **1** is rapidly catenated by irradiating **1** in an aqueous solution (Scheme 1b,c).

Scheme 1



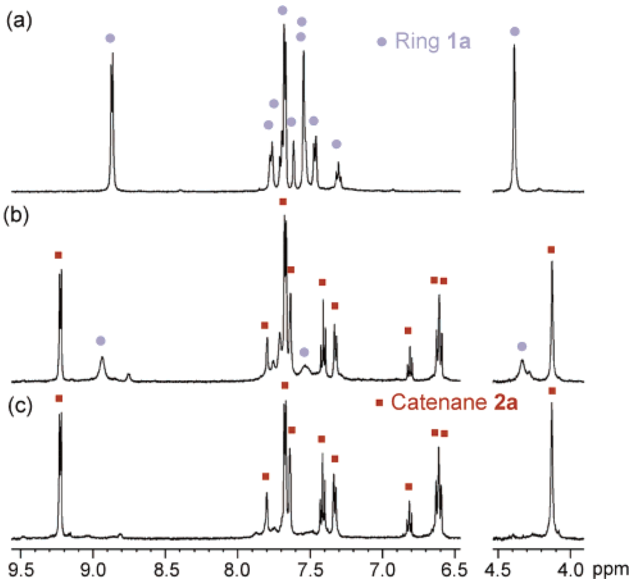


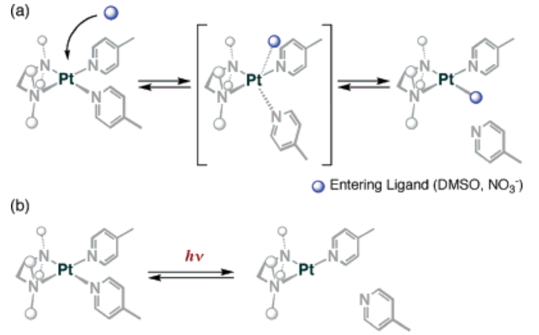
Figure 1. ^{1}H NMR observation of the catenation of Pt(II)-ring **1a** by UV-irradiation (500 MHz, DMSO-d_6/D$_2$O 1:2): (a) before irradiation, and after irradiation for (b) 5 min and (c) 15 min.

Only a few reports have described the photodissociation of Pt(II)−py coordination bonds, where the dissociation is monitored by subsequent ligand substitution or isomerization.[4,5] We anticipate that, in the absence of any other ligands, the photodissociation is immediately followed by a re-coordination process, which has been often considered as an unfavorable side reaction in previous studies.[6] As a result, a pyridyl ligand can be reversibly coordinated to platinum upon irradiation. On the basis of this idea, Pt(II)-ring **1** was irradiated in an aqueous medium in expectation of rapid catenation via the Pt(II)−py bond dissociation. Thus, Pt(II)-clipped coordination ring **1a** was prepared from (en)Pt(NO$_3$)$_2$ and the corresponding ligand according to the procedure described previously.[2] A DMSO-d_6/D$_2$O (1:2) solution of **1a** (2 mM) was irradiated at room temperature with an ultra-high-pressure Hg lamp filtered by a band-path glass filter (330 ± 70 nm).[7] Upon irradiation, the signals for **1a** disappeared gradually along with the appearance of new signals for catenane **2a**. The conversion was very rapid and, only after 15 min, **2a** was quantitatively formed (Figure 1b,c). The spectra of both **1a** and **2a** are qualitatively identical to those of Pd(II) analogues reported previously.[2,8] Cold-spray ionization mass spectrometry (CSI-MS) measurement[9] confirmed the formation of **2a** as evident from prominent signals that fully agreed with **2a**: for example, m/z 618.3 $[\mathbf{2a}-(\mathrm{NO_3}^-)_4+(\mathrm{dmso})_7]^{4+}$ and 740.8 $[\mathbf{2a}-(\mathrm{NO_3}^-)_3+(\mathrm{dmso})_3]^{3+}$.

Without irradiation, the once formed catenane **2a** is "locked" and not allowed to dissociate into separate rings even in a nonaqueous solvent. In fact, when dissolved in MeCN/MeOH (1:1), catenane **2a** remained unchanged and the dissociation was not observed despite the absence of effective hydrophobic interaction between the two rings. Of course, smooth dissociation into the component rings takes place if **2a** is "unlocked" in a nonaqueous solvent. Upon irradiation in MeCN/MeOH (1:1), **2a** disappeared

10.1021/ja067132y CCC: $37.00 © 2007 American Chemical Society

Scheme 2



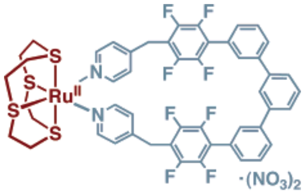
in 10 min, and component ring **1a** was formed in a high yield (Figure S8).[10]

The photoinduced catenation of **1a** was shown to be much faster than the thermally induced system. On heating **1a** at 90 °C in DMSO-d_6/D_2O (1:2), the Pt(II)−py bond was thermally unlocked, and **1a** was gradually converted to **2a** (Figure S1). However, it took a few days to equilibrate the reaction.[11]

The kinetic study of the catenation elucidated the mechanism of ligand substitution at the Pt(II) center. Analogous coordination ring **1b** with a sterically demanding *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (tmen), instead of en in **1a**, was prepared, and the rate constant for catenation was compared with that of **1a**. The kinetic measurement was done by monitoring the thermal catenation of **1a**,**b** by ^{1}H NMR at 90 °C in DMSO-d_6/D_2O (1:2). Under these conditions, the reactions roughly obeyed pseudo-first-order kinetics and the rate constant of the catenation of **1a** was estimated to be three times as high as that of **1b** (1.6×10^{-5} s^{-1} and 0.51×10^{-5} s^{-1} for **1a** and **1b**, respectively) (Figure S6). The significant difference in the rate constant is consistent with an associative mechanism via a pentacoordinated intermediate (Scheme 2a), where the sterically hindered tmen ligand destabilizes the intermediate.[12] In striking contrast, the rate constant for the photoinduced catenation was almost the same for both **1a** and **1b** (1.7×10^{-4} s^{-1} and 1.4×10^{-4} s^{-1}, respectively) under irradiation at 310 nm (6.8 mW) using Xe lamp equipped with monochromator (Figure S7). No influence of the steric demand of tmen ligand on the reaction rate is a strong indication that the photosubstitution proceeds via a dissociative mechanism (Scheme 2b) rather than the associative mechanism.[4,5]

Furthermore, the time-dependent calculation of a simplified model structure, $[(en)Pt(pyH)_2]^{2+}$, with the DFT B3LYP level of theory also supports the photolabilization. The calculated energy of electronic transition reasonably agrees with the experimental one in acetonitrile, in which an absorption band around 305 nm is ascribed to a HOMO−LUMO transition. Because LUMO is dominated by the character of antibonding $d_{x^2-y^2}$ orbital (Figure S12),[13] the excitation with a UV light should weaken the Pt(II)−py coordination bond.

Since the ligand photodissociation is a well-known process for Ru(II) complexes,[6,14] we examined the similar photoinduced catenation of Ru(II)-clipped coordination ring **3**. The Ru(II)-ring **3** was obtained by complexation of *cis*-[Ru([12]aneS$_4$)(H_2O)(dmso)](NO_3)$_2$ ([12]aneS$_4$ = 1,4,7,10-tetrathiacyclododecane)[15] and the bis(4-pyridyl)-appended ligand in methanol. As expected, the quantitative formation of a catenated dimer was observed by ^{1}H NMR and CSI-MS by irradiating the solution of **3** in DMSO-d_6/D_2O (1:2) for 45 min (Figure S9).



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In conclusion, we have achieved the reversible catenation of Pt(II)-clipped coordination rings based on the “photoswitchable molecular lock” concept. This concept has potential applications for the construction of a variety of Pt(II)-linked discrete 3D architectures, the frameworks of which self-assemble under irradiation and freeze under off-irradiation.

Supporting Information Available: Experimental details, spectroscopic data of **1**, **2**, **3**, **4**, and DFT calculation of $[(en)Pt(pyH)_2]^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA067132Y