

Synthesis of Metal Complexes Aiming to Convert between Chemical Energy and Electrical One

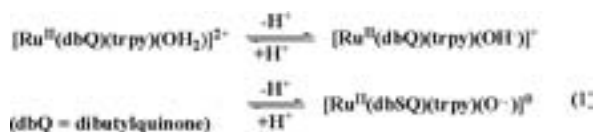
Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry



TANAKA, Koji
WADA, Tohru
OZAWA, Hironobu
KOSHIYAMA, Tamami
FUKUSHIMA, Takashi
TSUKAHARA, Yuhei
YAMAGUCHI, Yumiko
NAKAGAKI, Shizuka

Professor
Assistant Professor
IMS Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Graduate Student
Secretary
Secretary

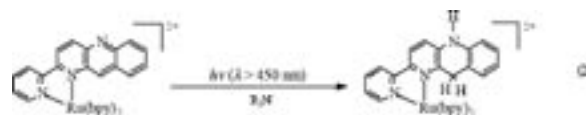
Metal ions involved in various metal proteins play key roles to generate metabolic energies through redox reactions of organic molecules. Metal complexes that have an ability to oxidize organic molecules at potentials more negative than reduction of dioxygen are feasible energy converter between chemical energy and electrical one. Some of high valent Ru=O complexes obtained by sequential proton and electron loss of the corresponding aqua-Ru complexes are proven to be active for the oxidation of organic molecules. However, the oxidation potentials of those aqua complexes to prepare high valent Ru=O ones are too positive to use as an energy transducer. We have succeeded smooth conversion from aqua to oxo ligands on Ru-dioxolene framework through proton coupled intramolecular electron transfer from the deprotonated form of the Ru–OH moiety to the dioxolene ligand (eq 1). The aqua-oxo



conversion using the unique redox behavior of Ru–dioxolene frameworks allowed us to isolate an unprecedented metal-oxo radical complex.

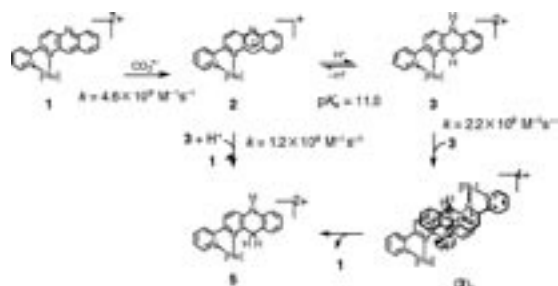
In addition to elucidation of the reactivity of Ru-oxyl radical complexes as electrocatalysts toward the oxidation of organic molecules, we are also aiming to develop multi-electron reduction of small inorganic molecules such as CO₂, N₂, and H₂O under mild reactions conditions, which would be key reactions to construct a renewable society. The difficulty in reductive activation of those molecules is attributable to the undesirable formation of high energy intermediates that are produced during stepwise one-electron transfer to the reaction centers. Recently, we showed that a mononuclear [Ru^{II}(pbn)(bpy)₂]²⁺ (bpy = 2,2'-bipyridine, pbn = 2-(2-pyridyl)benzo[b]-1,5-naphthyridine) ([1]²⁺) is smoothly converted to [Ru(pbnH₂)(bpy)₂]²⁺ ([1HH]²⁺) by not only electrochemical but also

photochemical reductions in the presence of proton (eq 2). Furthermore, the resultant [Ru(pbnH₂)(bpy)₂]²⁺ works as a functional model as the nicotinamide adenine dinucleotide NAD⁺/NADH redox reaction that plays a key role in a reservoir/source of two electrons and one proton in various biological energy transfer systems.



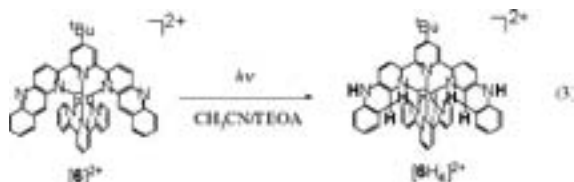
1. Photochemical and Radiolytic Production of an Organic Hydride Donor with a Ru^{II} Complex Containing an NAD⁺ Model Ligand

The Ru-pbn complex with an NAD⁺/NADH model ligand, [Ru(bpy)₂(pbn)]²⁺ ([1]²⁺), which acts as a catalyst in the electrochemical reduction of acetone to 2-propanol, similar to the enzymatic NAD⁺/NADH. The complex [1]²⁺ undergoes the reversible pbn^{-•}/pbn redox reaction at -0.72, V versus SCE in CH₃CN, which shows pH dependent (59 mV/pH) between pH 2 and 11 in H₂O, indicating the occurrence of one-electron reduction coupled with a proton-transfer reaction. The excited state of [1]²⁺ was reductively quenched by an amine to produce the one-electron-reduced species in dry organic solvents. The one-electron-reduced species is a pbn ligand radical anion and is stable in CH₃CN. On the other hand, continuous photolysis (λ > 300 nm) of a CH₃CN/triethanolamine (TEOA) solution (4 : 1, v/v) containing [1](PF₆)₂ produced [(1)HH]²⁺ with a quantum yield of 0.21 at λ = (355 ± 6) nm. Single crystals of [(1)HH](PF₆)₂·2CH₃CN is similar to that of [1]²⁺ except for the pbn and pbnH₂ ligands. Elongation of the C8–C10 and C8–C12 bonds of [(1)HH]²⁺ (1.510(4) and 1.498(6)) compared with those of [1]²⁺ (1.376(10) and 1.399(9)) demonstrates the



Scheme 1. The mechanism for photochemical two-electron reduction of $[1]^{2+}$.

formation of the 1,4-dihydropyridine framework in the pbnHH ligand (eq 2). Reduction of $[1]^{2+}$ by $\text{CO}_2^{\cdot-}$ is first order in the concentration of $[1]^{2+}$ and the protonation is very fast in a pH range from 3 to 13. A bimolecular decay of the transient species $[(1)H]^{2+}$ reveals that the species reacts via disproportionation to form $[1]^{2+}$ and $[(1)HH]^{2+}$. Thus, the photochemical reduction of $[1]^{2+}$ produces $[(1)HH]^{2+}$ without accompanying undesirable the carbon-centered radical–radical coupling of $[1]^+$ or $[H(1)]^{2+}$ radicals because of the steric interaction associated with the bulky $\{\text{Ru}(\text{bpy})_2\}$ moiety. The photochemical two-electron reduction of $[1]^{2+}$ is reasonably explained by Scheme 1. The initial step is one-electron reduction of $[1]^{2+}$ by $\text{CO}_2^{\cdot-}$ affording (2), and the following rapid protonation of the nitrogen atom (3). The resultant neutral pbnH[•] radical ligand (3) forms a π – π complex ((3)₂). The subsequent electron coupled proton transfer or hydrogen atom

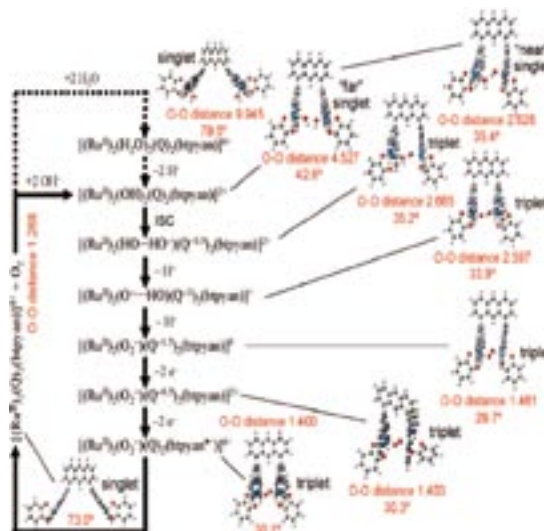


transfer from one neutral pbnH[•] to another one in the π – π complex produces the equimolar amount of $[1]^{2+}$ and $[1HH]^{2+}$. The finding of the photochemical two-electron reduction through disproportionation affording an equimolar amount of the oxide and two-electron reduced forms (Scheme 1) opens a new era for the photochemical multi-electron reduction of metal complexes, since the repeat of the photochemical two-electron reduction of the pbn moiety allowed smooth photochemical four-electron reduction of an analogous $[\text{Ru}(\text{bbnp})]$ (trpy)²⁺ (bbnp = 2,6-bis(benzo[b]-1,5-naphthyridin-6-yl)-4-*tert*-butylpyridine) under illumination of visible light in $\text{CH}_3\text{CN}/\text{TEOA}$ by (eq 3).

2. Water Oxidation by a Ruthenium Complex with Noninnocent Quinone Ligands: Possible Formation of an O–O Bond at a Low Oxidation State of the Metal

We have reported that a novel dinuclear Ru complex,

$[\text{Ru}_2(\text{OH})_2(3,6\text{-Bu}_2\text{Q})_2(\text{btpyan})](\text{SbF}_6)_2$ (3,6-Bu₂Q = 3,6-ditertbutyl-1,2-benzoquinone, btpyan = 1,8-bis-(2,2':6',2''-terpyridyl)-anthracene), that contains redox active quinone ligands and has an excellent electrocatalytic activity for water oxidation (TON > 35000) when immobilized on an ITO electrode (*Inorg. Chem.* **40**, 329–337 (2001)). The novel features of the dinuclear and related mononuclear Ru species with quinone ligands, and comparison of their properties to those of the Ru analogues with the bpy ligand (bpy = 2,2'-bipyridine) replacing quinone, are discussed together with new theoretical and experimental results that show striking features for both the dinuclear and mononuclear species. The identity and oxidation state of key mononuclear species, including the oxyl radical, have been reassigned. Gas-phase theoretical calculations indicate that the Ru-dinuclear catalyst seems to maintain predominantly Ru(II) centers while the quinone ligands and water moiety are involved in redox reactions throughout the entire catalytic cycle for water oxidation. Theoretical study identifies $[\text{Ru}_2(\text{O}_2^{\cdot-})(\text{Q}^{-1.5})_2(\text{btpyan})]^0$ as a



Scheme 2. The mechanism of eight-electron of water catalyzed by a Ru dinuclear complex.

key intermediate and the most reduced catalyst species that is formed by removal of all four protons before four-electron oxidation takes place. The over all reaction mechanism for the four-electron oxidation of water catalyzed by the dinuclear Ru complex is shown in Scheme 2.

References

- (a) D. Polansky, D. Cabelli, J. Muckerman, E. Fujita, T. Koizumi, T. Fukushima, T. Wada and K. Tanaka, *Angew. Chem., Int. Ed.* **46**, 5728–5730 (2007). (b) H. Tannai, T. Koizumi and K. Tanaka, *Angew. Chem., Int. Ed.* **46**, 7112–7115 (2007).
- (a) T. Koizumi and K. Tanaka, *Angew. Chem., Int. Ed.* **44**, 5891–5894 (2005). (b) J. Muckerman, D. Polansky, T. Wada, K. Tanaka and E. Fujita, *Inorg. Chem.* **47**, 3958–3968 (2008).