

A Synthetic NO reduction cycle on a bis(pyrazolato)-bridged dinuclear ruthenium complex including photo-induced transformation

Received 00th January 20xx,
Accepted 00th January 20xx

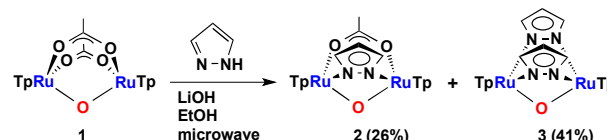
DOI: 10.1039/x0xx00000x

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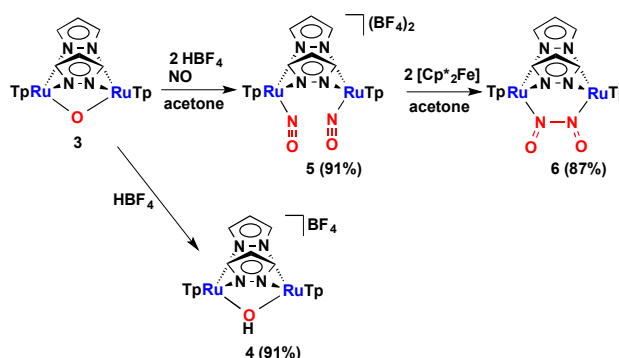
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A synthetic NO reduction cycle ($2\text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$) on a dinuclear platform $\{(\text{TpRu})_2(\mu\text{-pz})_2\}$ ($\text{Tp} = \text{HB}(\text{pyrazol-1-yl})_3$) was achieved, where an unusual N–N coupling complex was included. Moreover, an interesting photo-induced conversion of the N–N coupling complex to an oxido-bridged complex was revealed.

The reduction of nitric oxide (NO) to nitrous oxide (N_2O) is of great interest due to its relevance to global warming, because N_2O is a powerful greenhouse gas^{1a} and an ozone layer depletion agent.^{1b} Also, interestingly, in the human immune response, the reduction of increased NO occurs in order to protect us from nitrosative stress.² Their reduction are indispensable and controlled by NO reductase (NOR)³ and flavodiiron NO reductase (FDP)^{2b,4} in biological systems. Both the bacterial NOR and FDP enzymes possess dinuclear iron centers which would play a role in not only managing the redox reaction, but also arranging two NO molecules in adequate positions. Although the detailed mechanism has not been elucidated, the production of N_2O means that the N–N coupling of two NO molecules on metals would be a pivotal step. In 2007, we reported the N–N coupling on a dinuclear ruthenium complex, where an unusual neutral ($\text{O}=\text{N}-\text{N}=\text{O}$) form is revealed for the first time.⁵ And the use of the N–N coupling complex has achieved a NO reduction cycle ($2\text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$) in three steps.⁶ In one of the three steps, proton-assisted N_2O elimination, the mechanism has been proposed by DFT calculations, where a key finding is that the formation of a hyponitrite intermediate in the presence of proton(s) significantly reduces the activation barrier.⁷ However, the isolation of other N–N coupling complexes with the neutral



Scheme 1 Preparation of a bis(μ -pyrazolato) complex **3**. $\text{Tp} = \text{HB}(\text{pyrazol-1-yl})_3$.



Scheme 2 Synthetic scheme of a N–N coupling complex **6**. $\text{Tp} = \text{HB}(\text{pyrazol-1-yl})_3$.

($\text{O}=\text{N}-\text{N}=\text{O}$) form has not been reported yet. Herein, we report the second example of an N–N coupling complex, which achieves a NO reduction cycle. Interestingly, in the cycle, proton-assisted N_2O elimination did not proceed, but we found that photochemical N_2O elimination can be easily induced.

To prepare a bis(μ -pyrazolato) dinuclear ruthenium complex with Tp ($\text{Tp} = \text{HB}(\text{pyrazol-1-yl})_3$), we selected bis(μ -acetato)(μ -oxido) diruthenium $\{(\text{TpRu})_2(\mu\text{-O}_2\text{CMe})_2(\mu\text{-O})\}$ (**1**)⁸ as a starting material. The treatment of **1** with excess pyrazole in the presence of excess LiOH in EtOH under microwave heating for 2.5 h followed by column chromatographic purification afforded a mono(μ -pyrazolato) complex $\{(\text{TpRu})_2(\mu\text{-O}_2\text{CMe})(\mu\text{-O})(\mu\text{-pz})\}$ (**2**) (26% yield) and a bis(μ -pyrazolato) complex $\{(\text{TpRu})_2(\mu\text{-O})(\mu\text{-pz})_2\}$ (**3**) (41% yield) (Scheme 1). When a similar reaction was performed in EtOH under reflux, a longer reaction time (27 h) was necessary for obtaining **3** in a similar yield. Complex **3** was also prepared from the reaction of **2** with

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† Electronic Supplementary Information (ESI) available: Experimental and spectroscopic details for all new compounds, X-ray crystal structures of **2** and **4'**, cyclic voltammogram of **5**, and X-ray structural data for complexes **2**, **3**- CH_2Cl_2 , **4'**-ether, **5**, and **6**-thf. CCDC reference numbers 1832738–1832742. See DOI: 10.1039/x0xx00000x

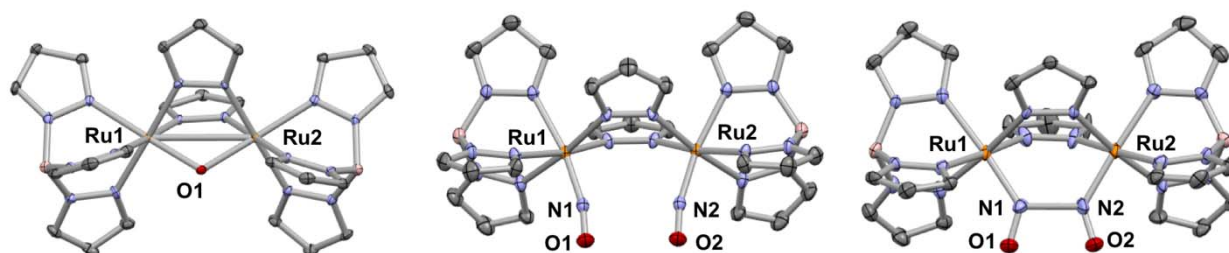


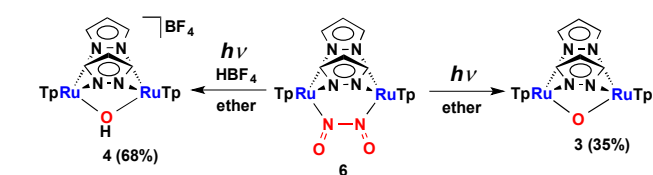
Fig. 1 Structures of **3** (left) and **6** (right) and the cation part of **5** (center) with ellipsoids drawn at the 50% probability level. The counter BF_4^- ions of **5**, crystallization solvents, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) are as follows. For **3**: Ru1–O1 1.904(3), Ru2–O1 1.897(3); Ru1–O1–Ru2 114.04(16). For **5**: Ru1–N1 1.755(5), O1–N1 1.147(6); Ru1–N1–O1 166.2(4). For **6**: Ru1–N1 1.884(5), Ru2–N2 1.912(6), O1–N1 1.234(7), O2–N2 1.202(8), N1–N2 1.801(7); Ru1–N1–O1 132.3(4), Ru2–N2–O2 134.0(4).

pyrazole and LiOH. The ^1H NMR spectra of **2** and **3** show diamagnetic signals assignable to four and three distinct sets of peaks of the pyrazolyl groups (Tp and bridging pyrazolyl ligands), indicating their C_s and C_{2v} symmetry, respectively. These structures are confirmed by single-crystal structural analyses (Fig. S1 (**2**) and Fig. 1 (**3**)).

A hydroxido-bridged dinuclear ruthenium complex $[(\text{TpRu})_2(\mu\text{-OH})(\mu\text{-pz})_2]\text{BF}_4$ (**4**) was easily obtained from the treatment of **3** with HBF_4 in diethyl ether (Scheme 2). The ^1H NMR spectrum of **4** shows paramagnetism due to the decrease of the antiferromagnetic coupling, which have been observed in the mono(μ -chlorido) analogue $[(\text{TpRu})_2(\mu\text{-Cl})(\mu\text{-OH})(\mu\text{-pz})]\text{BF}_4$.^{6b} Complex **4** was confirmed by its FAB-MS spectrum and the X-ray crystallographic analysis of the PF_6^- anion analogue (complex **4'**) (Fig. S1).

The nitrosylation of the bis(μ -pyrazolato) diruthenium complex **3** was carried out without the isolation of **4**. The exposure of an acetone solution of **3** to NO gas in the presence of HBF_4 gave rise to a dinitrosyl complex $[(\text{TpRu}(\text{NO}))_2(\mu\text{-pz})_2](\text{BF}_4)_2$ (**5**) in 91% yield (Scheme 2). The ^1H NMR spectrum of **5** indicates the retention of the C_{2v} symmetry. In the IR spectrum, a characteristic $\nu(\text{NO})$ band appears at 1918 cm^{-1} , which indicates the linear-type NO ligand.⁹ The FAB-MS spectrum exhibits the signal $[\text{M}+\text{BF}_4]^+$ at m/z 910.2, and moreover the structure of **5** was X-ray crystallographically confirmed (Fig. 1). Two $\text{TpRu}(\text{NO})$ fragments of **5** are bridged by two pyrazolato ligands. The N1–O1 bond distance (1.147(6) Å) and the Ru1–N1–O1 angle ($166.2(4)^\circ$) also support the linear-type NO ligand.

The desired N–N coupling complex was easily obtained by the two-electron reduction of **5**. The reaction of **5** with 2 equiv. of $[\text{Cp}^*_2\text{Fe}]$ gave $[(\text{TpRu})_2\{\mu\text{-N(=O)-N(=O)}\}(\mu\text{-pz})_2]$ (**6**) in 87% yield. Complex **6** was characterized by spectral data (NMR, IR, and FAB-MS), and the structure was confirmed by X-ray diffraction (Fig. 1). The N1–N2 distance (1.801(7) Å) is much longer than that of a typical N–N single bond (*ca.* 1.42 Å), but similar to that in the mono(μ -chlorido) analogue $[(\text{TpRu})_2(\mu\text{-Cl})-$



Scheme 3 Photo-induced transformation of a N–N coupling complex **6** to an oxido or a hydroxide complex. Tp = HB(pyrazol-1-yl)₃.

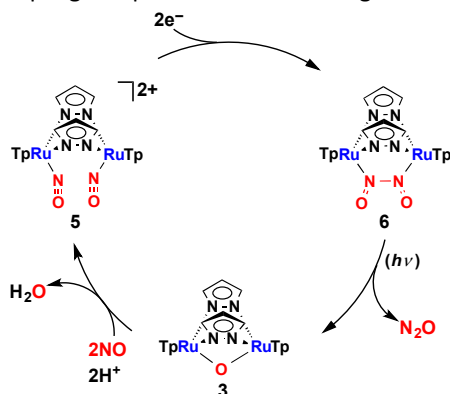
$\{\mu\text{-N(=O)-N(=O)}\}(\mu\text{-pz})]$ (1.861(3) Å).⁵ Moreover, the N–O bond distances of 1.234(7) and 1.202(8) Å exclude the formation of a known hyponitrite form.^{6a} The planarity within the N(=O)–N(=O) moiety is confirmed by the torsion angle, O1–N1–N2–O2 = $-0.5(5)^\circ$. The reversibility of this N–N bonding was supported by the cyclic voltammogram (Fig. S2), which features by a quasi-reversible two-electron redox couple at 0.25 V ($E_{1/2}$ vs. Ag/AgCl), which is lower than that of the mono(μ -chlorido) analogue (0.39 V).⁵ The two-electron redox process from **5** to **6** was confirmed by the controlled potential coulometry.

Since the proton-assisted elimination of N_2O of the N–N coupling complex has been achieved in the mono(μ -chlorido) diruthenium system,⁵ we tried the treatment of **6** with protic acids (HBF_4 or HOTf) in CH_2Cl_2 . The isolated complex was not the desired oxido-bridged complex **3**, but the dinitrosyl complex **5**, which indicates that the oxidation reaction occurred. To proceed with the elimination of N_2O , the photo-induced transformation of the N–N coupling complex was carried out (Scheme 3). A similar light-induced N_2O production of the dinitrosyl dinuclear complex has been reported.^{4b} After the irradiation of a diethyl ether solution of **6** for 2 h and evaporation, the crystallization of the residue reformed complex **3** in 35% yield. In the presence of $\text{HBF}_4\cdot\text{Et}_2\text{O}$, the irradiation afforded the hydroxide-bridged complex **4** in 68% yield, indicating the protonation of the oxido complex **3** which was generated *in situ*. In this reaction, the evolution of N_2O was detected by gas chromatography (4.9% yield based on the isolated **4**). This success motivated us to check the photo-induced conversion of the mono(μ -chlorido) analogue $[(\text{TpRu})_2(\mu\text{-Cl})\{\mu\text{-N(=O)-N(=O)}\}(\mu\text{-pz})]$. The irradiation of a diethyl ether solution of the mono(μ -chlorido) N–N coupling complex,⁵ followed by the addition of $\text{HBF}_4\cdot\text{Et}_2\text{O}$, also gave the

hydroxide-bridged complex $[(\text{TpRu})_2(\mu\text{-Cl})(\mu\text{-OH})(\mu\text{-pz})]\text{BF}_4$ (76% yield).^{6b} From the photochemical reaction the evolution of N_2O was detected. Interestingly, a sufficient conversion of the N–N coupling complex **6** to the oxido-bridged complex **3** was observed in toluene- d_8 at 100 °C for 3 days, but a similar conversion in the mono(μ -chlorido) analogue was not. According to the DFT calculations in the proton-assisted N_2O elimination,⁷ the proton(s) attached to the NO ligands withdraw two electrons from the Ru(II)–Ru(II) core to fix the electronic structure of $\text{Ru(III)}_2\text{-(N}_2\text{O}_2\text{)}^{2-}$, which is supported by the frontier orbitals. Thus, the excitation from the HOMO to LUMO by light irradiation may trigger the N_2O elimination.

Conclusions

We could achieve the synthetic NO reduction cycle ($2\text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$) including the unusual N–N coupling complex **6** (Scheme 4). This cycle comprises the nitrosation of the oxido-bridged complex using 2H^+ and NO, subsequent two-electron reduction of the resulting dinitrosyl complex affording the N–N coupling complex, and interesting photo-induced conversion of the N–N coupling complex to the oxido-bridged complex.



Scheme 4 Synthetic NO reduction cycle on a bis(pyrazolato)-bridged dinuclear ruthenium complex. Tp = HB(pyrazol-1-yl)₃.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the JSPS, KAKENHI grant number JP17K05813, and by the priority research project of Nagasaki University. We are grateful to Y. Tsujita, A. Utsunomiya, and S. Katamine at Nagasaki University for their technical assistance. We also thank Dr. H. Tanaka (Daido University) for helpful discussions.

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