

NO Reduction Cycle on Dinuclear Ruthenium Complexes having Hydrotris(pyrazolyl)borato

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Abstract

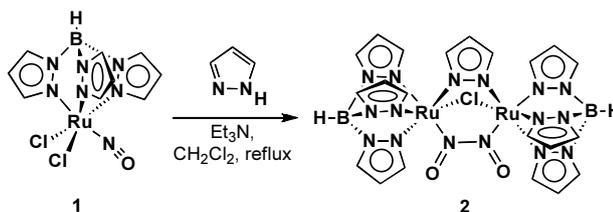
Bacterial nitric oxide reductase (NOR), which is a component of denitrification process in the global nitrogen cycle, catalyzes the reduction of NO to nitrous oxide (N₂O) ($2 \text{ NO} + 2 \text{ e}^- + 2 \text{ H}^+ \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$). On our continuing researches of nitrosylruthenium, we found N–N coupling of the two nitrosyl ligands on dinuclear rutheniums. Moreover, use of **2** achieved stepwise reproduction of the NOR catalytic process.

Introduction

Nitric oxide (NO) is vital to biological system as a signaling molecule in physiological properties and a component of denitrification process in the global nitrogen cycle. In the latter, metalloenzyme, bacterial nitric oxide reductase (NOR) catalyze the reduction of NO to nitrous oxide (N₂O) ($2 \text{ NO} + 2 \text{ e}^- + 2 \text{ H}^+ \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$). Active sites of NOR compose of close-arranged heme/non-heme diiron active center. On our continuing researches of nitrosylruthenium with hydrotris(pyrazolyl)borate (Tp) ligand, we found N–N coupling of the two nitrosyl ligands on dinuclear rutheniums. It is proposed that such N–N coupling would be a key step in the NOR catalytic process.

Experimental

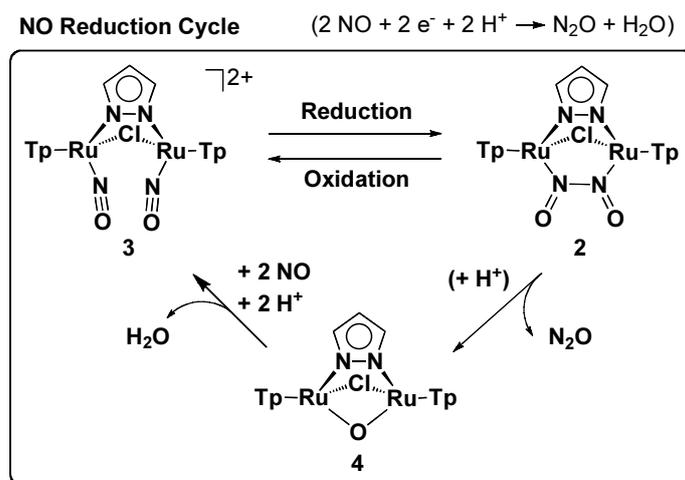
The N–N coupled complex (TpRu)₂(μ-Cl)(μ-pz){μ-N(=O)-N(=O)-} (**2**) were prepared from the reaction of TpRuCl₂(NO) (**1**) with pyrazole in the presence of Et₃N (Scheme 1). Complex **2** was



Scheme 1.

treated with AgBF_4 to give $[\{\text{TpRu}(\text{NO})\}_2(\mu\text{-Cl})(\mu\text{-pz})](\text{BF}_4)_2$ (**3**) in 56% yield. Complex **3** was treated with Zn powder afforded complex **2** in 70% yield.

Complex **2** was transformed into oxo-bridged dinuclear complex $(\text{TpRu})_2(\mu\text{-Cl})(\mu\text{-pz})(\mu\text{-O})$ (**4**) (21% yield) besides **3** (43% yield), by treatment with $\text{HBF}_4\cdot\text{OEt}_2$ in CH_2Cl_2 . Concomitantly, the evolution of N_2O was gas-chromatographically detected. Complex **4** was protonated by $\text{HBF}_4\cdot\text{OEt}_2$ to give hydroxo-bridged dinuclear complex $[(\text{TpRu})_2(\mu\text{-Cl})(\mu\text{-pz})(\mu\text{-OH})]\text{BF}_4$ (**5**) in 76%. Moreover, for **5**, additional protonation, followed by exposure to NO gas reproduced the complex **3** in 53%.



Results and Discussions

It was revealed that oxidation of the N–N coupled species **2** brought about cleavage of the N–N bond to give *cis*-dinitrosyl dinuclear form **3**, and also that on reduction this *cis*-dinitrosyl complex **3** cleanly reformed the N–N coupled species **2**. Interestingly, treatment of the N–N coupled complex **2** with the protic acid afforded the oxo-bridged dinuclear complex **4** with the evolution of N_2O . Moreover, double protonation of the oxo-bridged dinuclear complex **4**, followed by exposure to NO gas, regenerated the *cis*-dinitrosyl complex **3**, completing the reduction cycle. This indicates stepwise reproduction of the NOR catalytic process.

Conclusions

We achieved stepwise reproduction of the NOR catalytic process on dinuclear ruthenium complexes.

References

1. Y. Arikawa, T. Asayama, Y. Moriguchi, S. Agari, and M. Onishi, *J. Am. Chem. Soc.*, **129**, 14160-14161 (2007).