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Arikawa, Yasuhiro; Matsumoto, Naoki; Asayama, Taiki; Umakoshi, Keisuke; Onishi, Masayoshi

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Conversion of oxido-bridged dinuclear ruthenium complex to dicatonic dinitrosyl ruthenium complex using proton and nitric oxide: Completion of NO reduction cycle

Yasuhiro Arikawa,*a Naoki Matsumoto,a Taiki Asayama,a Keisuke Umakoshi,b and Masayoshi Onishi²

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The global nitrogen cycle has been a topic of great interest, where significant reactions have been performed by some metalloenzymes. The bacterial nitric oxide reductase (NOR) is a component of this cycle, particularly in the denitrification processes of anaerobic bacteria.¹ NORs catalyze the reduction of NO to N₂O with the consumption of 2 electrons and 2 protons (2NO + 2H⁺ + 2e⁻ → N₂O + H₂O). Despite the lack of structural data on these enzymes, their active site have been suggested to contain heme/non-heme dinuclear iron centers, which is similar to the active site of heme-copper oxidases. Also, the mechanism of action of NORs is a matter of debate.² However, in any cases, transformation of two molecules of NO to one molecule of N₂O indicates N-N coupling of two NO ligands on transition metals is key intermediate. Recently, excellent synthetic functional model complexes of NOR have been reported,³ and these complexes shows NOR activity (conversion of 2 NO to N₂O). But the conclusive evidence of N-N coupling of two NO ligands have not been obtained.

In our continuing research,⁴ we have found N-N coupling of NO ligands on dinuclear ruthenium complex, [(TpRu)(μ-Cl)(μ-pz)](μ-N(=O)N(=O)-κ²) (1),⁵ which is supported by Tp = hydrotris(pyrazolyl)borate ligands eqn (1)). The X-ray crystallographic analysis of the N-N coupled complexes shows that the unique N-N bond is much longer than that of a typical N-N single bond. Interestingly, the N-N bond was cleaved by chemical oxidation, affording dicatonic dinitrosyl complex [(TpRu(NO)₂(μ-Cl)(μ-pz)][BF₄]₂ (2), and reformed by chemical reduction, showing reversibility of the N-N bond. Moreover, treatment of 1 with the protic acid afforded oxido-bridged dinuclear ruthenium complex [(TpRu)(μ-Cl)(μ-O)(μ-pz)] (3) with evolution of N₂O, indicating NOR activity. In connection with this, we report here double protonation of 3 and subsequent treatment with NO, affording 2. This indicates completion of NO reduction cycle on dinuclear ruthenium complex.

Treatment of the oxido-bridged dinuclear ruthenium complex 3 with 1 equiv of HBF₄ in diethyl ether gave hydroxido-bridged dinuclear ruthenium complex [(TpRu)[μ-Cl(μ-OH)(μ-pz)]BF₄ (4) in 63% yield (Scheme 1). The H NMR spectrum of 4 indicates paramagnetism (see ESI†), although the NMR spectra of 3 show diamagnetic nature probably due to strong antiferromagnetic spin exchange coupling via a superexchange mechanism.⁶ Protonation of the oxido bridge in 3 would weaken the orbital overlap between the Ru dₓz and oxygen pₓ orbitals, resulting decrease of the antiferromagnetic coupling. The FAB-MS spectrum exhibits the parent molecular ion signal at m/z 748.1, showing one mass increment as compared with 3. Finally, the structure of...
was determined by single-crystal X-ray diffraction analysis (Fig. 1). Complex 4 has a C2 symmetry with the mirror plane passing through the bridged chlorido, hydroxido, and pyrazole’s center. Protonation on the bridged oxido ligand was confirmed by Ru1-O distance (2.0038(19) Å), which is longer than that of 4-bromopyrazolato- and oxido-bridged derivative of 3 (1.898(4), 1.904(3) Å). 4 It is also longer than Ru-O distances of bis(carboxylato)- and hydroxido-bridged dinuclear ruthenium complex [(TpRu)(μ-OOCCH3)2(μ-OH)]PF6 (1.957(3), 1.960(3) Å). 6

Moreover, additional protonation of 4 with HBF4, followed by anion exchange with acetone-d6 solution of HBF4, gave the dicationic dinitrosyl complex (Scheme 3).

In conclusion, protonation of the oxido-bridged dinuclear NaBF4, to afford dinuclear ruthenium [(TpRu)2(μ-Cl)(μ-OH)]PF6 (1.957(3), 1.960(3) Å). 6

Additional protonation of 4 should give aqua-bridged dinuclear ruthenium [(TpRu)(μ-OH)(μ-Cl)(μ-pz)](BF4)2 (5) (Scheme 2). In 1H NMR spectrum, when HBF4 was added to an acetone-d6 solution of 4, one set of paramagnetic signals, which would be assigned to 5, appeared. Isolation of 5 was failed, probably because of easy deprotonation. However, its formation in the reaction mixture was detected by FAB-MS spectroscopy (m/z 749.0). Thus, after treatment of 4 with HBF4 for 15h, the reaction mixture was exposed to NO to give 2 in 53% yield. On the other hand, 4 was allowed to react with NO without HBF4, followed by anion exchange with NaBF4, to afford 2 in 26% yield.

In conclusion, protonation of the oxido-bridged dinuclear complex 3 with HBF4 gave the hydroxido-bridged dinuclear complex 4. Moreover, additional protonation of 4 with HBF4, which generated the aqua-bridged dinuclear complex 5 in situ, followed by treatment with NO, gave the dicaticonic dimetosyl complex 2. Previous results and this success lead to completion of NO reduction cycle on dinuclear ruthenium complex (Scheme 3).

Scheme 3 NO reduction cycle (2NO + 2H+ + 2e− → N2O + H2O) on dinuclear ruthenium complex.

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Notes and references


