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

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The hydroxido-bridged dinuclear ruthenium complex 4, which is supported by Tp ligands, has been prepared from protonation of the oxido-bridged dinuclear ruthenium complex 3. Additional protonation of 4, affording the aqua-bridged dinuclear ruthenium complex 5 in situ, and subsequent treatment with NO gave rise to the dicaticonic dinitrosyl complex 2. These indicate completion of NO reduction cycle on dinuclear ruthenium complex.

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 has 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 NOR activity. In our continuing researches,4 we have found N-N coupling of two NO ligands have not been obtained.

In our continuing researches,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),4b 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 dicaticonic 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 1H 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.5 Protonation of the oxido bridge in 3 would weaken the orbital overlap between the Ru dσ and oxygen pπ 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

Fig. 1 Molecular structure of cation part of 4, with thermal ellipsoids at the 50% probability level. All hydrogen atoms, except for O-H, and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–Cl = 2.4401(10), Ru1–O = 2.0038(19), Ru1–Cl–Ru1* = 104.14(13).

Scheme 1

Scheme 2
In conclusion, protonation of the oxido-bridged dinuclear NaBF₄, to afford Additional protonation of which generated the aqua-bridged dinuclear complex followed by treatment with NO, gave the dicationic dinitrosyl complex. Previous results and this success lead to passing through the bridged chlorido, hydroxido, and was determined by single-crystal X-ray diffraction analysis with NO without HBF₄, followed by anion exchange with failed, probably because of easy deprotonation. However, its Ru-O distances of bis(carboxylato)- and hydroxido-bridged complexes with NO, gave the dicationic dinitrosyl species. Additional protonation of should give aqua-bridged dinuclear ruthenium complex ([TpRu]₂(μ-OOCCH₃)₂(μ-OH)PF₆)₂(1.957(3), 1.960(3) Å). 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 dimetisyl 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


