

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

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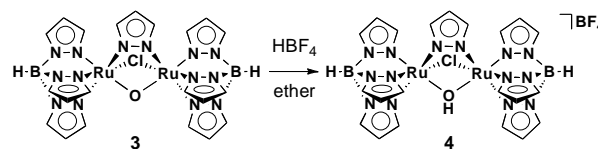
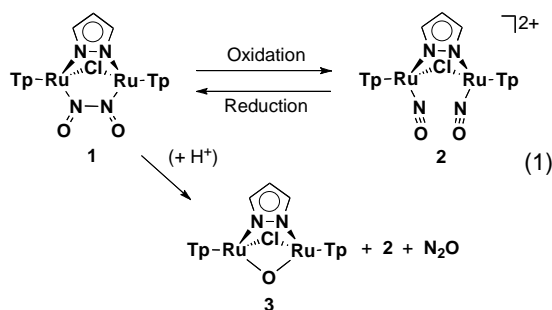
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The hydroxido-bridged dinuclear ruthenium complex **4**, which is supported by Tp ligands, has been prepared from protonation of the oxido-bridged dinuclear ruthenium complex **3**. Additional protonation of **4**, affording the aqua-bridged dinuclear ruthenium complex **5** in situ, and subsequent treatment with NO gave rise to the dicationic 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 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 researches,⁴ we have found N-N coupling of NO ligands on dinuclear ruthenium complex, [(TpRu)₂(μ-Cl)(μ-pz){μ-N(=O)-N(=O)-κ²}] (**1**),^{4a} 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 dicationic dinitrosyl



Scheme 1

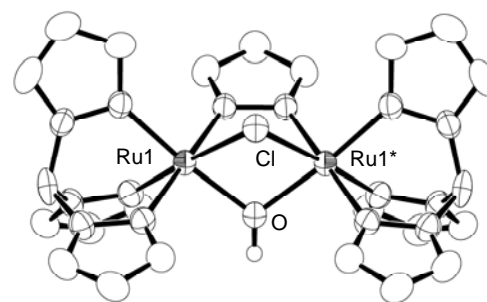
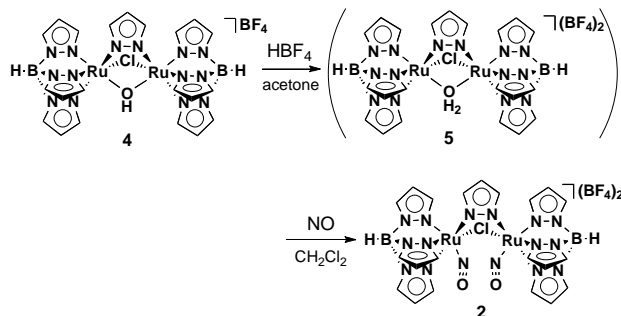


Fig. 1 Molecular structure of cation part of **4**, with thermal ellipsoids at the 50% probability level. All hydrogen atoms, except for O-H, and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–Cl = 2.4401(10), Ru1–O = 2.0038(19), Ru1–Cl–Ru1* = 80.74, Ru1–O–Ru1* = 104.14(13).

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)₂(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)₂(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 dπ 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

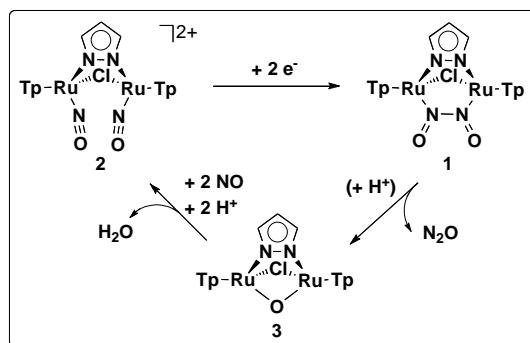
Scheme 2



4 was determined by single-crystal X-ray diffraction analysis (Fig. 1). Complex **4** has a C_s 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).^{4a} It is also longer than Ru-O distances of bis(carboxylato)- and hydroxido-bridged dinuclear ruthenium complex [(TpRu)₂(μ-OOCCH₃)₂(μ-OH)]PF₆ (1.957(3), 1.960(3) Å).⁶

Additional protonation of **4** should give aqua-bridged dinuclear ruthenium [(TpRu)₂(μ-OH₂)(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 dicationic dinitrosyl 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 ($2\text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$) on dinuclear ruthenium complex.

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Notes and references

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‡ Synthesis of **3**. To a CH₂Cl₂ (5.0 mL) solution of **1** (41.9 mg, 0.0513 mmol) was added HBF₄·OEt₂ (8.0 □l, 0.0584 mmol). The mixture was stirred for 30min at room temperature and filtered. The resulting orange solid was washed with CH₂Cl₂ and crystallized from CH₃CN/ether to give **2** (21.2 mg, 43%). On the other hand, the dark green filtrate and the washings were evaporated, and the residue was separated on column chromatography with a silica gel by use of CH₂Cl₂-acetone (40/1) as an eluent to give **3** (8.0 mg, 21%) from the blue band. Complex **3** is compared with the previously reported spectroscopic data for this species.^{4a}

§ Synthesis of **4**. A diethyl ether (7.0 mL) solution of **3** (47.3 mg, 0.0633 mmol) was treated with HBF₄·Et₂O (10 □L, 0.073 mmol) at room temperature. After stirring for 2 h, the resulting precipitate was filtered and washed with diethyl ether. Crystallization from acetone/diethyl ether gave **4** as dark red brown crystals (33 mg, 63%). IR (KBr, cm⁻¹): ν□BH) 2501 (m), ν□BF) 1119-1050 (s). FAB MS: *m/z* 748.1 [M]⁺. Anal. Calcd. for C₂₁H₂₄B₃ClF₄N₁₄ORu₂·C₄H₁₀O·C₃H₆O: C, 34.79; H, 4.17; N, 20.28. Found: C, 34.59; H, 3.91; N, 20.33. Crystal data. C₂₈H₄₀B₃ClF₄N₁₄O₃Ru₂, *M* = 966.73, monoclinic, *a* = 26.8810(17), *b* = 14.7534(8), *c* = 10.1208(8) Å, β = 97.1150(11)°, *U* = 3982.9(5) Å³, *T* = 296.1 K, space group *C2/m* (no. 12), *Z* = 4, 15144 reflections measured, 4622 unique (*R*_{int} = 0.021) which were used in all calculations. The final *R*(*F*²) was 0.0541 (all data).

¶ Synthesis of **2**. An acetone (5.0 mL) solution of **4** (25 mg, 0.030 mmol) was treated with HBF₄·Et₂O (8.0 □L, 0.0584 mmol) at room temperature. After stirring for 15 h, the reaction mixture was concentrated to dryness and redissolved in CH₂Cl₂ (7.0 mL). The solution was frozen, degassed, and backfilled with 1 atm of NO. The reaction mixture was stirred for 1 h, evaporated to dryness, and washed with diethyl ether. Crystallization from MeOH/diethyl ether gave **2** as red brown crystals (15 mg, 53%). Complex **2** is compared with the previously reported spectroscopic data for this species.^{4a}

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