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Reversible N−N Coupling of NO Ligands on Dinuclear Ruthenium Complexes and Subsequent N_2O Evolution: Relevance to Nitric Oxide Reductase

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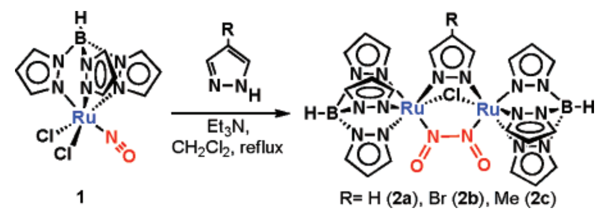
Transition metal-mediated transformations of nitric oxide (NO) have been biologically and environmentally attractive research fields in these decades. One biologically important subject is denitrification which constitutes one of the main key processes of the global biogeochemical nitrogen cycle, and in particular, bacterial NO reductase (NOR) has been described to catalyze the two-electron reduction of two NO molecules to nitrous oxide (N_2O) at bimetallic active sites (close-arranged heme/non-heme diiron active centers).[1] We have examined chemical reactivities of nitrosylruthenium supported by hydrotris(pyrazolyl)borate (Tp),[2] and accidentally 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. In a NO molecule, the *cis*-NO dimeric molecule with weak N···N interaction is present in its low-temperature solid state.[3] Lippard and Karlin have succeeded in the syntheses of closely related dinitrosyl diiron model complexes, but neither of them exhibits similar N−N coupling.[4] Furthermore, in our system, it was revealed that oxidation of this N−N coupled species brought about cleavage of the N−N bond to give *cis*-dinitrosyl dinuclear form, and interestingly also that on reduction this *cis*-dinitrosyl complex cleanly reformed the N−N coupled species.

Treatment of $TpRuCl_2(NO)$ (**1**: $\{RuNO\}^6$) with an equimolecular amount of pyrazole in the presence of excess Et_3N in refluxing CH_2Cl_2 gave rise to the dinuclear complex $(TpRu)_2(\mu\text{-Cl})(\mu\text{-pz})$ $\{\mu-\kappa^2\text{-N(=O)}-\text{N(=O)}\}$ (**2a**: $\{RuNO\}^7$) in 29% yield (Scheme 1). The use of 4-bromo or 4-methyl pyrazole afforded the corresponding dinuclear complexes (**2b**, Br−pz (25%); **2c**, Me−pz (ca. 15%)), while the use of 3,5- dimethylpyrazole did not. The IR spectra of **2** show much lower frequencies of ν(NO) bands (1605 (**2a**), 1608 (**2b**), and 1604 cm^{-1} (**2c**)) than that of **1** (1893 cm^{-1}). Their FAB-MS spectra show parent molecular ion signals with $[\mathbf{2}\text{-(NO)}]^+$ fragments, in support of their formulation. The ^1H NMR spectra of **2a** exhibit three sets of Tp−pyrazolyl groups and two resonances (1:2) of bridging-pyrazolyl protons, indicating its *Cs* symmetry.

The structures of **2b** and **2c** were confirmed by single-crystal X-ray structural analyses, and the ORTEP view of **2c** is shown in Figure 1. Two TpRu fragments of **2c** are bridged by one chloride, one Me−pz, and the interesting part κ^2-*N*,*N*−N(=O)−N(=O) with a Ru−Ru distance of 3.5570(2) Å. The N−N distance (1.861(3) Å) is significantly shorter than that of *cis*-NO dimer (2.18 Å) in the low-temperature solid state,[3] but much longer than that of typical N−N single bond (ca. 1.42 Å).[5] To verify this N−N bond, DFT calculations starting from the X-ray structural data were performed, and the HOMO is revealed to bear N−N bonding character. Moreover, X-ray structural data of the N(=O)−N(=O) moiety indicate the N−O bond distances of 1.197(3) and 1.193(3) Å, excluding known hyponitrite form.[6] The Ru−N−O angles are 136.1(2) and 137.4(2)°. The planarity within the N(=O)−N(=O) moiety is confirmed by the torsion angle O1−N1−N2−O2 = 4.7-(2)°.

Scheme 1



The aforementioned reaction condition has been optimized, while the reaction mechanism is still unclear.[7] The use of 3 equiv of pyrazole led us to isolate [TpRuCl(pzH)(NO)]Cl (**3a**: $\{RuNO\}^6$) (ca. 52% yield).[8] Taking account of the formal neutral N(=O)−N(=O) bridge in **2**, $2e^-$ reduction occurred during the formation of **2**. This reductive formation was probably associated with the presence of the excess Et_3N, which is essential to the preparation of **2**.[9]

To characterize the unusual N(=O)−N(=O) bridge, chemical oxidation of **2a** was carried out. Complex **2a** was allowed to react with $AgBF_4$ in CH_3CN, affording $[\{TpRu(NO)\}_2(\mu\text{-Cl})(\mu\text{-pz})](BF_4)_2$ (**4a**·$(BF_4)_2$: $\{RuNO\}^6$) in 56% yield (Scheme 2). Complex **4a**·$(BF_4)_2$ was also obtained from oxidation reaction of **2a** with $[Cp_2Fe]BF_4$. The ^1H NMR spectrum of **4a**·$(BF_4)_2$ indicates the retention of the *Cs* symmetry. In the IR spectrum, a characteristic ν(NO)

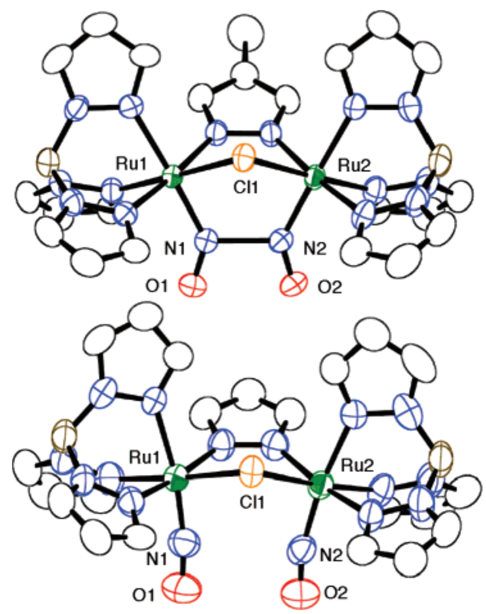


Figure 1. Molecular structures of **2c** (top) and **4a** (bottom), H-atoms are not shown. Toluene solvent molecule and BF_4 counterions in the structures of **2c** and **4a**·$(BF_4)_2$, respectively, are omitted.

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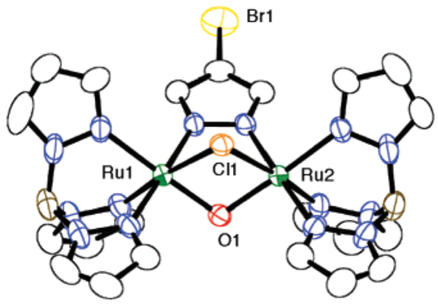
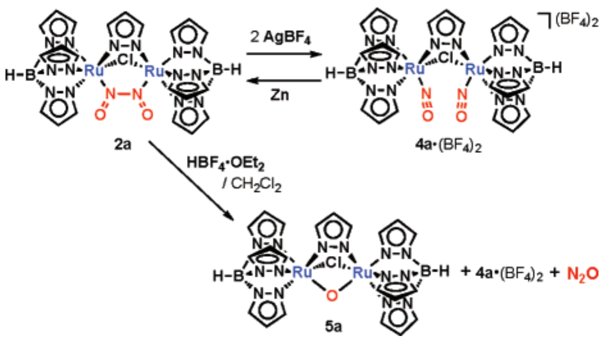


Figure 2. Molecular structure of **5b**, H-atoms are not shown. $CHCl_3$ solvent molecules in the structure of **5b** are omitted.

Scheme 2



band appears at 1930 cm^{-1}, which is comparable to that of **1**. The FAB-MS spectra exhibit the signal [**4a** + BF_4^-]$^+$ at m/z 878.1, and moreover the structure of **4a**·$(BF_4)_2$ was X-ray crystallographically confirmed.

The crystal structure of **4a**·$(BF_4)_2$ (Figure 1) verified the presence of two {TpRu(NO)} units bridged by chloride and pyrazolate, accompanied by two BF_4^-. Bonding interaction between two NO nitrogen atoms is no longer observable as exemplified by N···N separation of 3.006(8) Å. The N−O bond distances are 1.169(9) and 1.131(8) Å, and expansion of the Ru−N−O angles (169.7(6) and 165.4(6)°) compared with those of **2b** and **2c** is evident. Comparison of **4a**·$(BF_4)_2$ with **2b** and **2c** clearly shows the shortening of the Ru−NO bond lengths.

Oxidation of **2a** induced cleavage of the N−N bond. The reversibility of this N−N bonding was supported by the cyclic voltammogram of **2a**, which is featured by a reversible two-electron redox couple at 0.389 V ($E_{1/2}$ vs Ag/AgCl).[10] Actually, reductive treatment of **4a**·$(BF_4)_2$ with Zn cleanly reformed complex **2a** (70% yield).

Isolation of **2** led us to inquire as to whether N_2O can be produced from **2** and then the corresponding oxo-bridged dinuclear complex can be formed similarly to the proposed mechanism for the NOR catalytic cycle.[1] To check this possibility, we preliminarily examined the reaction conditions and found that complex **2a** was transformed into the oxo-bridged dinuclear complex $(TpRu)_2(\mu\text{-Cl})(\mu\text{-pz})(\mu\text{-O})$ (**5a**) (21% yield) besides **4a**·$(BF_4)_2$ (43% yield), by treatment with HBF_4·OEt_2 in CH_2Cl_2 (Scheme 2).[11] Concomitantly, the evolution of N_2O was gas-chromatographically detected.[12] Unfortunately, the yields of complex **5a** and the evolved N_2O gas were relatively low in these reaction conditions. Complex **5a** was characterized by spectral data (NMR, IR, and EI-MS) and elemental analysis, and the structure was confirmed by the X-ray diffraction observation of the bromo derivative **5b** (Figure 2).

In conclusion, we have communicated an example of unprecedented N−N coupling of the two nitrosyl ligands on dinuclear complexes, which is proposed as a critical step in the NOR catalytic cycle.[1] It is remarkable that this N−N bond is easily cleaved by oxidation and regenerated again by reduction. Interestingly, transformation of the N−N coupled complexes into the oxo-bridged dinuclear complexes with the evolution of N_2O was observed. This observation would provide significant information regarding the mechanism of NO reduction to N_2O by NOR. Studies to find the optimized reaction conditions for generation of the oxo-bridged complexes and evolution of the N_2O gas and also to complete the NO reduction cycle like NOR are currently underway.

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Supporting Information Available: Full experimental and spectroscopic details for all new compounds, ORTEP drawing of **2b**, depiction of HOMO for the calculated complex **2c**, cyclic voltammetry diagram of **2a**, and X-ray structural data for complexes **2b**, **2c**, **4a**, and **5b** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) For Ru-complex, see: Böttcher, H.-C.; Graf, M.; Mereiter, K.; Kirchner, K. *Organometallics* **2004**, *23*, 1269−1273.

(7) The reaction is complicated, and several other uncharacterized complexes were also produced.

(8) Complex **3a** was contaminated by trace amounts of inseparable impurities.

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(10) Two-electron redox between **2a** and **4a** was confirmed by their peak separation between oxidation and reduction waves in the cyclic voltammogram and also by their controlled potential coulometry.

(11) In the protonation reaction of **2a**, it seems that protonated species on the bridging oxygen atom of **5a** would be formed, and then removal of the proton would occur in the step of chromatographic separation to release **5a**.

(12) N_2O was detected in 25% yield on the basis of the separated complex **5a**; that is, about $^1/_4$ mole of N_2O gas per 1 mole of **5a**.

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