resolved band splitting of 9 cm^{-1} for the mixed-valent system does not signify valence localization but occurs similarly for the mononuclear iron(II) complex **5** (Table 1). Most importantly, there is no specific aromatic ring vibration band visible in the IR spectrum between 1500 and 1700 cm^{-1} for the mixed-valent state. This would indicate loss of inversion symmetry (nonzero dipole moment) and thus (partial) valence localization, as has been observed for pyrazine-bridged analogues.[5, 12]

The *g* factor component pattern of $(NEt_4)_5$(**4**) in the EPR spectrum at $g = 2.531$, 2.422, and 1.794 is similar to the results observed for other $Fe^{II}(L)Fe^{III}$ systems.[5, 10, 13] This supports the formulation of a mixed-valent diiron complex with little direct participation of the ligands in the spin distribution.

By using 1,2,4,5-tetrazine as a superior π-acceptor bridging ligand, we have been able to obtain an unprecedentedly stable new cyanodiiron(2.5) coordination compound with an extraordinary solvent dependence[14]—a link between the numerous well-known ammineruthenium complexes[11b] and Prussian Blue.[1]

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[8] $(NEt_4)_3$(**5**)·$2H_2O$: $(NEt_4)_6$(**4**)·$2H_2O$ (50 mg, 0.039 mmol) dissolved under dissociation in acetonitrile (60 mL). Addition of solid NEt_4CN (10 mg, 0.064 mmol), removal of the solvent, and repeated chromatography on Sephadex LH20 in water yielded a dark blue powder which was treated with acetone (10 mL) in an ultrasonic bath at room temperature. The solid residue was dried under vacuum (8 mg, 30% $(NEt_4)_3$(**5**)·$2H_2O$). Elemental analysis calcd for $C_{31}H_{66}FeN_{12}O_2$ (694.80 $g\,mol^{-1}$): C 53.59, H 9.58, N 24.19; found: C 53.28, H 9.28, N 23.04%. The complex is stable in air as a solid and in solution, both in water and aprotic solvents. ^1H NMR (D_2O): $\delta = 10.25$ (d, 1H), 9.18 (d, 1H); $J = 2.6$ Hz.
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Conversion of Molecular Oxygen into a Hydroperoxo Species by Ring-Opening Protonation of a Cyclic η^2-Peroxo Intermediate: Characterization of the η^2-Peroxo and Hydroperoxo Complexes**

Yoshiaki Takahashi, Mariko Hashimoto, Shiro Hikichi, Munetaka Akita,* and Yoshihiko Moro-oka*

Transition metal–dioxygen species are key intermediates in catalytic oxygenation reactions such as synthetic and metabolic transformations.[1] Since the oxygen atoms of cyclic

[*] Prof. Dr. M. Akita, Prof. Dr. Y. Moro-oka,
Dr. Y. Takahashi, M. Hashimoto, Dr. S. Hikichi
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, 4259 Nagatsuta
Midori-ku, Yokohama 226-8503 (Japan)
Fax: (+81) 45-924-5226
E-mail: makita@res.titech.ac.jp

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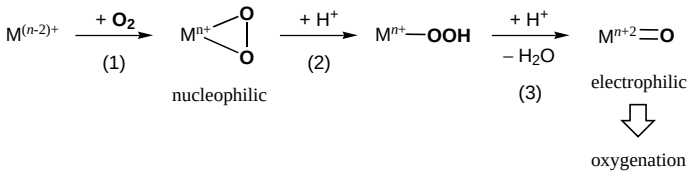
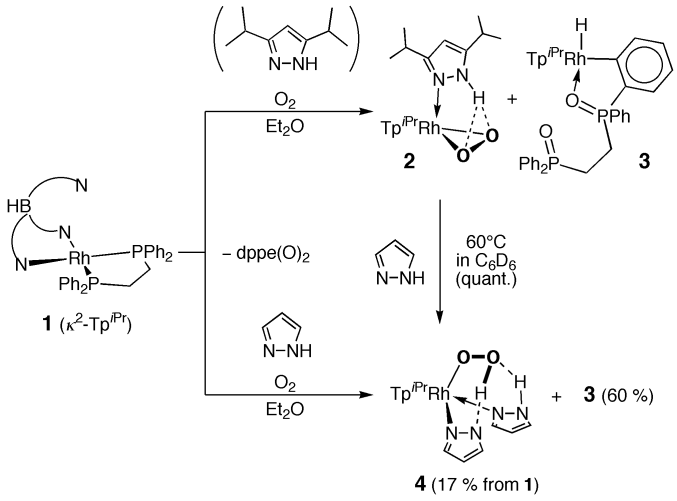
η^2-peroxo intermediates, which are formed by the oxidative addition of a dioxygen molecule to a low valent metal species (step 1 in Scheme 1), are normally nucleophilic, such intermediates do not show remarkable oxygenation activity. Therefore the η^2-peroxo intermediates need to be activated in some way prior to oxygenation. In the well-studied cytochrome P-450 system it is proposed that protonation of the η^2-peroxo intermediate gives the η^1-hydroperoxo species (step 2), which is further converted into the high valent, highly electrophilic oxo intermediate by protonation followed by the elimination of water (step 3).[2] However, no concrete structural evidence for these steps has been reported so far.[3] During the course of the systematic synthetic study on dioxygen complexes based on the Tp^R systems[4,5] we have found that molecular oxygen can be converted into a hydroperoxo species, that is: 1) oxygenation of a Rh^I precursor affords the Rh^{III}-peroxo and -hydroperoxo species, and 2) the formation of the latter species involves a ring-opening protonation of the former η^2-peroxo intermediate, which corresponds to step 2.



Scheme 1. Activation of molecular oxygen by a transition metal species.

Stirring an ethereal solution of the square-planar Rh^I-dppe complex $[(Tp^{iPr})Rh(dppe)]$ (**1**)[5, 6] under an O_2 atmosphere afforded a mixture of products, from which the O_2 adduct **2** was isolated as yellow crystals in a low yield (1.4%) together with dppe dioxide and the cyclometalated hydride complex **3** (52%; Scheme 2). Complex **2** contained the 3,5-di-2-propylpyrazole ($pz^{iPr}H$) ligand from the partial decomposition of the Tp^{iPr} ligand, and oxygenation of **1** in the presence of $pz^{iPr}H$ improved the yield of **2** up to 23%, while that of **3** remained virtually unaffected (51%).



Scheme 2. Oxygenation of $[(Tp^{iPr})Rh(dppe)]$ (**1**) to give η^2-peroxo and hydroperoxo complexes (**2** and **4**, respectively).

Coordination of an O_2 molecule in **2** is evidenced by the O-O vibration observed at 848 cm^{-1} in the IR spectrum and the FD-MS data ($m/z = 752$ $[M^+ = \mathbf{1}+O_2+pz^{iPr}H - dppe]$) (FD = field desorption). The ^1H NMR spectrum of **2** contains three sets of pyrazolyl signals in a 1:1:2 ratio, which suggests a structure with mirror symmetry as well as the incorporation of one molecule of $pz^{iPr}H$. The B–H vibration appearing at 2540 cm^{-1} in the IR spectrum indicates a κ^3-coordination of the Tp^{iPr} ligand.[7] The octahedral hexacoordinated structure suggested by the spectral data has been confirmed by X-ray crystallographic analysis (Figure 1 a).[8] The O–O (1.467(5) Å) and Rh–O bond lengths (2.013(3) and 2.001(4) Å) are comparable to those of the previously reported octahedral $[Rh(\eta^2\text{-}O_2)]$ complexes[9] and clearly indicate that the coordinated O_2 is present as a peroxo ligand (O_2^{2-}). The N···O distances (O1···N42: 2.681(6) Å, O2···N42: 2.733(6) Å) and the orientation of the pyrazole ring lead to the conclusion that a hydrogen-bonding interaction is present between the peroxo oxygen atoms and the pyrazole nitrogen atom (N42). The NH hydrogen atom, which was refined isotropically, is actually located in the middle of the three atoms (O1, O2, and N42). The deshielded NH signal ($\delta = 12.42$) in the ^1H NMR spectrum and the obscured NH vibration in the IR spectrum are in accord with this structural description. In the isostructural Mn complex $[(Tp^{iPr})Mn(pz^{iPr}H)(O_2)]$ (**5**, O–O: 1.43(1), Mn–O: 1.841(9), 1.878(8), N···O: 2.82(2), 2.99(2) Å),[10] however, the hydrogen-bonding interaction is unsymmetrical and weaker than that in **2**. The $pz^{iPr}H$ moiety in the Mn complex **5** becomes dissociated from the metal center upon dissolution, whereas the Rh complex **2** retains the structure in solution. The strong interaction in **2** is probably a result of the highly basic O_2 ligand, which arises from the effective back-donation from the Rh center.

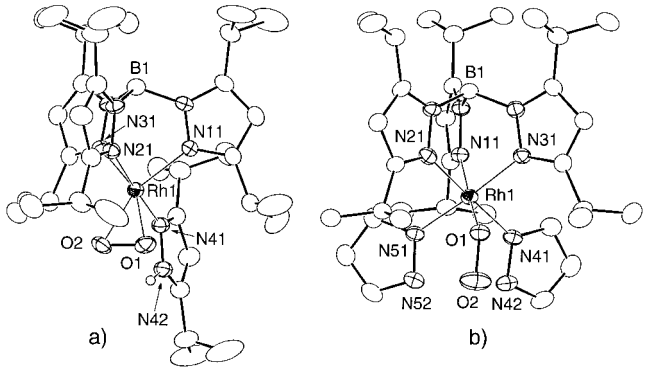


Figure 1. Molecular structures of **2** a) and **4** b) drawn at the 30% probability level.

The cyclometalated complex **3** was characterized by the δ(Rh–H) and ν(Rh–H) absorptions in the NMR and IR spectra, respectively, and X-ray crystallographic analysis.[8] Formation of **3** suggests that another Rh^I intermediate, namely $[(Tp^{iPr})Rh\{dppe(O)_2\}]$ (**B** in Scheme 3), is the direct precursor to **2**.

Since an external $pz^{iPr}H$ molecule was incorporated into the O_2 complex **2** (Scheme 2), the additive effect of another donor was examined. Oxygenation of **1** in the presence of the

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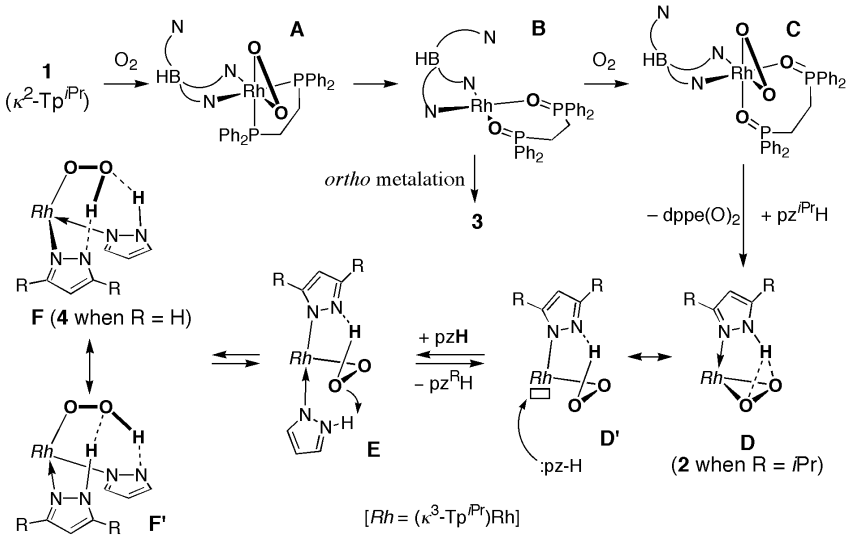

Scheme 3. Plausible mechanism for the formation of **2** and **4**.

unsubstituted pyrazole afforded yellow crystals of **4** (17% yield) and the metallacycle **3** (Scheme 2). The FD-MS data ($m/z = 736$) of **4** suggested another peroxo complex that was formulated as $[(Tp^{iPr})Rh(pzH)_2(O_2)]$. However, X-ray crystallographic analysis (Figure 1b) revealed the structure was actually the hydroperoxo complex $[(Tp^{iPr})Rh(OOH)(pz)(pzH)]$.[8] Examples of structurally characterized hydroperoxo complexes are still very rare,[11] and complex **4** is only the second hydroperoxorhodium complex following the mixed metal Ir–Rh complex $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}pz)_3Rh(OOH)(dppe)]$ (**6**, Rh–O: 2.021(5), O–O: 1.432(8) Å).[11a] The O–O distance in **4** (1.413(8) Å) falls in the typical range of those reported for peroxo and hydroperoxo complexes including **2** and **6**,[1, 11] though the Rh–O bond (1.994(4) Å) is slightly shorter than that in **2** and **6**. In this case, too, the N···O and N···N distances (O2–N42: 2.85(1) Å; O2–N52: 2.857(8) Å; N42–N52: 2.78(1) Å) and the orientation of the O_2 and pz groups indicate the presence of hydrogen-bonding interactions between the O2, N42, and N52 atoms. Although the positions of the hydrogen atoms cannot be determined by X-ray crystallography,[12] they should be located between the O2 and N42 atoms and between the O2 and N52 atoms as suggested by their ^{1}H NMR data and the obscured O–H and N–H vibrations. The ^{1}H NMR chemical shift ($\delta = 12.03$ (2H)) is comparable to the δ(NH) value for **2** with the NH···O hydrogen bond, and the two hydrogen atoms remain equivalent even at $-90\,^\circ$C. The symmetry observed in the NMR spectrum and crystallographic features suggest the contribution of the two canonical structures **F** and **F′** (Scheme 3) to both the solution and solid-state structures.

The results reported in this communication can be interpreted in terms of the mechanism summarized in Scheme 3. Oxygenation of **1** should initially produce the simple O_2 adduct $[(Tp^{iPr})Rh(\eta^2\text{-}O_2)(dppe)]$ (**A**), which is readily converted into **B** by oxygenation of the coordinated dppe ligand. In contrast to other $[(Tp^{iPr})Rh(L_2)]$-type complexes (L_2 = diene, $(olefin)_2$, $(CO)_2$), which are inert toward O_2,[6, 7] complex **1** with the electron-donating dppe ligand is readily susceptible to O_2 oxidative addition. Subsequent orthometalation of the phosphane oxide ligand in **B** gives **3**,[13] while some of **B** further reacts with an O_2 molecule (→**C**) to furnish the isolable O_2 adduct **D** (**2**) after elimination of $dppe(O)_2$ and coordination of $pz^{iPr}H$. In the case of the 3,5-di-2-propyl derivative (R=*i*Pr), only one $pz^{iPr}H$ molecule can be coordinated to the Rh center as a consequence of the steric hindrance of the bulky 2-propyl substituents and, therefore, the reaction is terminated at this stage. The coordinatively unsaturated resonance structure **D′** should contribute to the final structure. A less bulky substrate such as pyrazole (R = H) can be further coordinated to the vacant site in **D′** to give the bis-pz adduct **E**, which is converted into the final product **F**(**4**) after reorganization of the hydrogen-bonding interactions. Since the octahedral $[(Tp^{iPr})Rh]$ complexes are usually inert with respect to the ligand displacement,[6] the hydrogen-bonding interaction must assist the incorporation of the second pz^RH molecule.

In accord with this mechanism, heating a $[D_6]$benzene solution of **2** with an excess of pyrazole at 60 °C resulted in the quantitative formation of **4** (Scheme 2); the bulky $pz^{iPr}H$ ligand in **2** is replaced by pzH, and **4** should be formed through incorporation of a second pzH molecule followed by a reorganization. The replacement of the $pz^{iPr}H$ ligand reveals that the incorporation of pz^RH is a reversible process. It is remarkable that, as a result of the hydrogen-bonding interaction, both of the complexes **2** and **4** presented herein are sufficiently stable to survive chromatographic purification on silica gel.

In conclusion, we reveal that 1) oxygenation of the Rh^I precursor **1** produces the Rh^{III}-peroxo and -hydroperoxo complexes **2** and **4**, respectively, and 2) the OOH functional group in **4** results from ring-opening protonation of the O_2 ligand in **2**. These transformations can be viewed as the first structural evidence for the key steps of the O_2 activation by a transition metal species and conversion of molecular oxygen into a hydroperoxo species (steps 1 and 2 in Scheme 1). It should also be noted that the hydrogen-bonding interactions play pivotal roles in the formation and stabilization of **2** and **4** and similar assistance may be viable in the O_2 activation by metalloproteins.

Experimental Section

2 and **3**: A solution of $\mathbf{1}\cdot 0.5\,Et_2O$ (458 mg, 0.456 mmol) and 3,5-di-2-propylpyrazole (66 mg, 0.434 mmol) in diethyl ether (20 mL) was stirred under an O_2 atmosphere (1 atm) for 18 h. After removal of the precipitated colorless solid (dppe dioxide) by filtration through a celite pad the volatiles were removed under reduced pressure. The resulting residue was subjected to chromatography on silica gel. Elution with diethyl ether gave **3** (80 mg, 23%) as a pale yellow solid and subsequent elution with THF gave **2** (232 mg, 51%) as a yellow solid. **2**: ^{1}H NMR (selected data, 200 MHz, $CDCl_3$, 25 °C): $\delta = 12.42$ (br s, 1H; NH), 5.88 (s, 2H; 4-pz^{iPr} in Tp^{iPr}), 5.75 (d, $^3J(H,H) = 2.4$ Hz, 1H; 4-pz^{iPr} in additional $pz^{iPr}H$), 5.66 (s, 1H; 4-pz^{iPr} in

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Tp^{iPr}); IR (KBr): $\tilde{\nu} = 2540$ (BH), 848 cm^{-1} (OO); FD-MS: m/z: 752 [M^+]. **3**: ^1H NMR $\delta = 5.70$, 5.68, 5.67 (s × 3, 1H × 3; 4-pz^{iPr} in Tp^{iPr}), −16.86 (d, $^1J(Rh,H) = 17.5$ Hz, 1H; RhH); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): $\delta =$ 57.5, 31.8 (d × 2, $^3J(P,P) = 48$ Hz). IR $\tilde{\nu} = 2534$ (BH), 2082 cm^{-1} (RhH); FD-MS: m/z: 998 [M^+].

4: A solution of **1** · 0.5 Et_2O (490 mg, 0.485 mmol) and pyrazole (67 mg, 0.984 mmol) in diethyl ether (15 mL) was stirred under an O_2 atmosphere (1 atm) for 17 h. After removal of the precipitated colorless solid (dppe dioxide) by filtration through a celite pad the volatiles were removed under reduced pressure and the residue was separated by column chromatography on silica gel. Elution with diethyl ether and THF gave **4** as a yellow solid (62 mg, 17%) and **3** (291 mg, 60%), respectively. **4**: ^1H NMR: $\delta =$ 12.03 (br s, 2H; N-H-O), 7.77, 6.89 (d × 2, $^3J(H,H) = 2.0$ Hz, 2H × 2; 3,5-pz), 6.20 (t, 2H, $^3J(H,H) = 2.0$ Hz; 4-pz), 5.88 (s, 2H; 4-pz^{iPr}), 5.79 (s, 1H; 4-pz^{iPr}); IR (KBr): $\tilde{\nu} = 2539$ cm^{-1} (BH); FAB-MS: m/z: 736 [M^+].

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[5] Abbreviations used in this communication: Tp^{iPr} = hydrotris(3,5-di-2-propylpyrazolyl)borate; Tp^R = hydrotris(substituted-pyrazolyl)-borate; pz = pyrazolyl, pz^{iPr} = 3,5-di-2-propylpyrazolyl; dppe = ethane-1,2-diylbis(diphenylphosphan).

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[8] X-ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated $Mo_{K\alpha}$ radiation at −60 °C. The structures were solved by a combination of the direct methods (SHELXS 86) and DIRDIF. Least-squares refinements were carried out using SHELXL 93 linked to teXsan (single crystal structure analysis software, version 1.9, Molecular Structure Corporation, The Woodlands, TX, **1985** and **1992**). Crystal data for **2**: $C_{36}H_{62}N_8O_2BRh$, $M_r = 752.7$, monoclinic, space group $P2_1/a$, $a =$ 19.834(3), $b = 9.719(1)$, $c = 21.68(1)$ Å, $\beta = 106.81(3)°$, $V =$ 4000(2) Å^3, $Z = 4$, $\rho_{calcd} = 1.25$ g cm^{-3}, $\mu = 4.7$ cm^{-1}, $R1 = 0.0676$ (on F^2) for the 6317 unique data ($wR2 = 0.1887$ for all 6810 data) with $F > 4\sigma(F)$ and 453 parameters. Crystal data for **3** · 2 toluene: $C_{67}H_{86}N_6O_2BP_2Rh$, $M_r = 1183.12$, triclinic, space group $P\bar{1}$, $a =$ 15.095(5), $b = 16.875(5)$, $c = 12.649(3)$ Å, $\alpha = 91.71(3)$, $\beta = 97.66(3)$, $\gamma = 89.66(2)°$, $V = 3191(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.23$ g cm^{-3}, $\mu = 3.6$ cm^{-1}, $R1 = 0.096$ (on F^2) for the 8866 unique data with $F > 4\sigma(F)$ ($wR2 =$ 0.2360 for all 10380 data) and 672 parameters. Crystal data for **4** · 0.5 OEt_2 · 2 MeCN: $C_{39}H_{65}N_{12}O_{2.5}BRh$, $M_r = 855.7$, triclinic, space group $P\bar{1}$, $a = 13.542(6)$, $b = 14.107(2)$, $c = 12.859(6)$ Å, $\alpha =$ 113.09(3), $\beta = 98.39(4)$, $\gamma = 81.46(3)°$, $V = 2224(1)$ Å^3, $Z = 2$, $\rho_{calcd} =$ 1.28 g cm^{-3}, $\mu = 4.3$ cm^{-1}, $R1 = 0.0725$ (on F^2) for the 7578 unique data with $F > 4\sigma(F)$ ($wR2 = 0.2063$ for all 8068 data) and 525 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-118496 (**2**), -118497 (**3**), -118498 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] Because X-ray crystallography suggested intermolecular hydrogen-bonding interactions (O2 ··· N42*: 2.978(9) Å, O2 ··· N52*: 2.92(1) Å), location of the hydrogen atoms would be disordered among the O and N atoms. Another possible structure with mirror symmetry contains one hydrogen atom in the middle of the O2, N42, and N52 atoms and the other bonded only to the O2 atom, but apparently it is not consistent with the spectral data.

[13] The formation of **3** is an irreversible process.