Characterization of a Dinuclear (μ-Hydroxo)(μ-pyrazolato)dimanganese(II) Complex and Hydrolytic Equilibrium of the Bridging Pyrazolate Ligand

Hidehito Komatsuzaki,[†,‡] Shinobu Ichikawa,[‡] Shiro Hikichi,*[,†] Munetaka Akita,[†] and Yoshihiko Moro-oka*[,†]

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, and Department of Chemistry and Material Engineering, Ibaraki National College of Technology, 866 Nakane, Hitachinaka 312-8508, Japan

Received December 29, 1997

Introduction

Hydrotris(pyrazolyl)borates (=Tp^R; R denotes substituents of the pyrazolyl rings) are widely used as monoanionic 6e-donating ligands for the synthesis of many inorganic and organometallic compounds.[1] Also, pyrazoles and their deprotonated forms (=pyrazolate anion) themselves are known to serve as aromatic N donor ligands.[2] In our laboratory, the first- and second-row transition metal complexes with a series of Tp^R ligands have been investigated as biomimetic models and organometallic compounds. In several cases, however, additional coordination of a pyrazole ligand was observed.[3] One of the remarkable examples of the additional-pyrazole-containing complexes is the mononuclear Mn(III) side-on peroxo complex $Tp^{Pr^i_2}Mn(O_2)$(3,5-Pr^i_2pzH) (**1**: $Tp^{Pr^i_2}$ = hydrotris(3,5-diisopropylpyrazolyl)borate; 3,5-Pr^i_2pzH = 3,5-diisopropylpyrazole),[3a] which shows thermochromism according to the formation of the hydrogen bond between the pyrazole NH and the peroxide. This peroxo complex **1** is prepared by the reaction of the dinuclear Mn(II) bis(μ-hydroxo) complex $Tp^{Pr^i_2}Mn(\mu\text{-}OH)_2MnTp^{Pr^i_2}$ (**2**) with H_2O_2 in the presence of 2 equiv of 3,5-Pr^i_2pzH, although, in the absence of the pyrazole, the dinuclear Mn(III) bis(μ-oxo) complex $Tp^{Pr^i_2}Mn(\mu\text{-}O)_2MnTp^{Pr^i_2}$ (**3**)[4] is formed instead of **1** (Scheme 1). Therefore interaction of **2** with 3,5-diisopropylpyrazole should be involved as a key step for the formation of **1**. Herein we report the details of the reaction of **2** with 3,5-Pr^i_2pzH and the result of the oxygenation of the obtained dinuclear (μ-hydroxo)(μ-pyrazolato)dimanganese(II) complex will be also described.

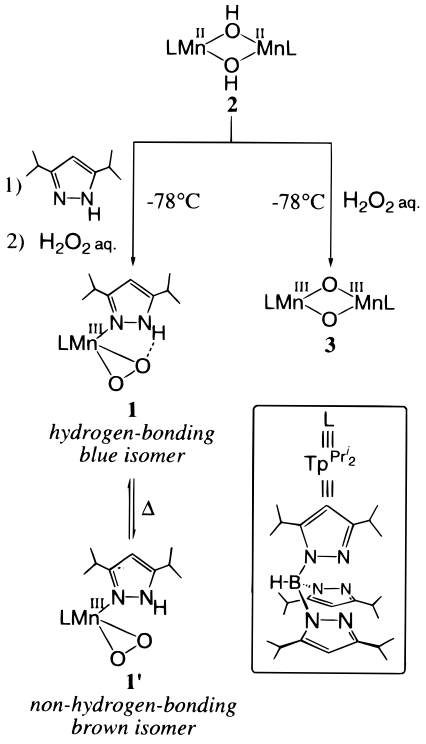
Experimental Section

Instrumentation. IR measurements were carried out as KBr pellets using a JASCO FT/IR-5300 spectrometer. Electron impact and field desorption mass spectra were recorded on a Hitachi M-80 mass spectrometer. UV−vis spectra were recorded on a Shimadzu UV-260 spectrometer. The X-ray data collections were performed on a Rigaku four-circle AFC-5S diffractometer. The X-ray data analysis was completed by the teXsan structure solving program system on an Indigo-IRIS computer (Silicon Graphics), obtained from Rigaku.

Materials and Methods. All solvents used were purified by the literature methods.[5] The reagents of the highest grade commercially available were used without further purification. All manipulations were performed under argon by standard Schlenk techniques. The dinuclear Mn(II) bis(μ-hydroxo) complex, $Tp^{Pr^i_2}Mn(\mu\text{-}OH)_2MnTp^{Pr^i_2}$ (**2**),[4] the Mn(II) chlorido complex, $Tp^{Pr^i_2}MnCl$,[4] and 3,5-diisopropylpyrazole[6] were prepared by the methods described previously. Sodium 3,5-diisopropylpyrazolate was prepared by treatment of 3,5-diisopropylpyrazole with NaH in THF.

Synthesis of $Tp^{Pr^i_2}Mn(\mu\text{-}OH)(\mu\text{-}3,5\text{-}Pr^i_2pz)MnTp^{Pr^i_2}$ (4). A 1 equiv amount of 3,5-diisopropylpyrazole (13 mg; 0.087 mmol) was added to a toluene solution (7 mL) of $Tp^{Pr^i_2}Mn(\mu\text{-}OH)_2MnTp^{Pr^i_2}$ (**2**), (93 mg; 0.087 mmol), and this reaction mixture was stirred for 30 min. Then 1 g of Na_2SO_4 was added, and the reaction mixture was stirred for an additional 30 min. After removal of the solid by filtration, the colorless solution was evaporated under vacuum. An IR spectrum of the crude product showed no peak at 3712 cm^{-1} arising from the starting bis(μ-hydroxo) complex **2**. The resulting white product was washed three times with MeCN by decantation and then dried under vacuum (82 mg; 0.068 mmol; 79% yield based on **2**). Anal. Calcd for $C_{63}H_{108}N_{14}OB_2Mn_2$: C, 62.58; H, 9.00; N, 16.22. Found: C, 62.22; H, 8.90; N, 16.12. IR (KBr pellet, ν/cm^{-1}): 3684 (OH), 2542 (BH). FD-MS (*m*/*z*): 153 (3,5-Pr^i_2pzH), 1072 ($Tp^{Pr^i_2}Mn(\mu\text{-}O)_2MnTp^{Pr^i_2}$ (**3**)[4]), 1086 ({Mn[HB(3-$OCMe_2$-5-Pr^ipz)(3,5-Pr^i_2pz)$_2$]}$_2$(μ-O) (**6**)[7]), 1101

Scheme 1



[†] Tokyo Institute of Technology.
[‡] Ibaraki National College of Technology.

(1) Recent reviews are the following: (a) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (c) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291. (d) Reger, D. L. *Coord. Chem. Rev.* **1996**, *147*, 571.
(2) (a) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115. (b) Steel, J. P. *Coord. Chem. Rev.* **1990**, *106*, 227.
(3) (a) Kitajima, N.; Komatsuzaki, K.; Hikichi, S.; Osawa, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1994**, *116*, 11596. (b) Kitajima, N.; Osawa, M.; Tamura, N.; Moro-oka, Y.; Hirano, T.; Hirobe, M.; Nagano, T. *Inorg. Chem.* **1993**, *32*, 1879. (c) Hikichi, S.; Ogihara, T.; Fujisawa, K.; Kitajima, N.; Akita, M.; Moro-oka, Y. *Inorg. Chem.* **1997**, *36*, 4539.
(4) Kitajima, N.; Singh, U. P.; Amagai, H.; Osawa, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7757.
(5) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.
(6) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277.

S0020-1669(97)01622-4 CCC: $15.00
Published on Web 06/25/1998

($Tp^{Pr^i_2}Mn(\mu\text{-}CO_3)MnTp^{Pr^i_2}$ [8]). Reaction of 2 equiv of 3,5-diisopropylpyrazole (39 mg; 0.255 mmol) and **2** (136 mg; 0.127 mmol) (Mn:pyrazole = 1:1) under the same conditions also resulted in the yielding of **4** (136 mg; 0.113 mol; 89% yield).

Reaction of the (μ-Hydroxo)(μ-pyrazolato)dimanganese(II) Complex 4 with an Excess Amount of 3,5-Pr^i_2pzH. A 4.9 equiv amount of 3,5-diisopropylpyrazole (108 mg; 0.706 mmol) was added to a toluene solution (10 mL) of **4** (174 mg; 0.144 mmol), and this reaction mixture was stirred for 30 min at room temperature. Then 1 g of Na_2SO_4 was added to the reaction mixture, which was then stirred for an additional 30 min. After removal of the solid by filtration, the solvent was evaporated under vacuum.

Preparation of the Pyrazolato Complex 5 by Reaction of the Mn(II) Chlorido Complex with the Sodium Salt of the Pyrazolate Anion. A 1.1 equiv amount of sodium 3,5-diisopropylpyrazolate (70 mg; 0.401 mmol) was added to a CH_2Cl_2 solution (5 mL) of $Tp^{Pr^i_2}MnCl$ (208 mg; 0.374 mmol), and this reaction mixture was stirred for 2 h at room temperature. After removal of solid by filtration, the solvent was evaporated under vacuum. Formation of the desired pyrazolato complex **5** was confirmed by EI-MS spectroscopy data of the resulting white solid (m/z = 672), which corresponded to the molecular weight of $Tp^{Pr^i_2}Mn(3,5\text{-}Pr^i_2pz)$. Attempted crystallization from a CH_2Cl_2 solution of the crude solid of **5** resulted in isolation of the colorless block crystals of **4**.

Reaction of the (μ-Hydroxo)(μ-pyrazolato)dimanganese(II) Complex 4 with H_2O_2. A 60 equiv amount of aqueous H_2O_2 (30 wt %, 0.2 mL; 5.88 mmol) was added to a toluene solution (10 mL) of **4** (116 mg; 0.096 mmol), and this reaction mixture was stirred for 20 min at room temperature. The remaining aqueous H_2O_2 was frozen by cooling the reaction mixture at −78 °C. After removal of the ice (i.e. the remaining aqueous H_2O_2) by filtration at −78 °C, the solvent was evaporated under vacuum. The resulting solid was recrystallized from MeCN at −20 °C (62.4 mg; 0.089 mmol; 46% yield). The brown product was identified as the non-hydrogen-bonding isomer of the mononuclear Mn(III) peroxo pyrazole complex **1′** by comparison with the data of an authentic sample which was prepared by the method described in ref 3a.

Reaction of the (μ-Hydroxo)(μ-pyrazolato)dimanganese(II) Complex 4 with O_2. A 10 mL toluene solution of **4** (199 mg; 0.165 mmol) was stirred under O_2 (1 atm) for 24 h. FD-MS analysis of the resulting solution indicated the formation of the dinuclear Mn(III) bis(μ-oxo) complex **3** (m/z = 1072) and the ligand oxygenated complex $\{Mn[HB(3\text{-}OCMe_2\text{-}5\text{-}Pr^ipz)(3,5\text{-}Pr^i_2pz)_2]\}_2(\mu\text{-}O)$ (**6**, m/z = 1086). An IR spectrum of the products mixture obtained by removal of solvent under vacuum exhibited ν_{NH} absorption at 3199 cm^{-1} arising from 3,5-Pr^i_2pzH.

Reaction of the (μ-Hydroxo)(μ-pyrazolato) Complex 4 with H_2O. A 0.2 mL volume of H_2O was added to a 10 mL CH_2Cl_2 solution of **4** (43.8 mg; 0.036 mmol), and this solution was stirred for 1 h. Removal of the solvent and H_2O under vacuum yielded the white solid.

X-ray Data Collections and Structural Determinations. Crystals suitable for X-ray analysis of **4**·1.5C_5H_{12} were obtained from pentane solutions at −20 °C under argon atmosphere. The crystal was sealed in a thin-wall glass capillary to avoid the reaction with atmospheric O_2 and loss of the pentane molecules for crystallization. A Mo X-ray source equipped with a graphite monochromator (Mo Kα, λ = 0.710 680 Å) was used. Automatic centering and least-squares routines were carried out for all the compounds with 20 reflections of 20° < 2θ < 25° to determine the cell parameters. Data collections were completed with an $\omega-2\theta$ scan.

The structure of **4**·1.5C_5H_{12} was solved by direct methods (SAPI-91). Subsequent difference Fourier synthesis (DIRDIF) easily located all the non-hydrogen atoms, which were refined anisotropically except the pentane molecules. Neutral scattering factors were obtained from the standard source.[9] All hydrogen atoms except that attached to the oxygen atom were located at calculated positions and were not refined (d(C−H) = 0.95 Å with the isotropic thermal factor of U_{iso}(H) = 1.2U_{iso}(C)). The hydrogen atom of OH group was found in the Fourier difference map and refined isotropically. The cell parameters and data collection and refinement results are provided in Table 1. Full bond lengths, bond angles, atomic coordinates, and isotropic and anisotropic thermal parameters are available as Supporting Information.

Table 1. Crystal Data and Data Collection Details of $Tp^{Pr^i_2}Mn(\mu\text{-}OH)(\mu\text{-}3,5\text{-}Pr^i_2pz)MnTp^{Pr^i_2}$·1.5$C_5H_{12}$ (**4**·1.5C_5H_{12})

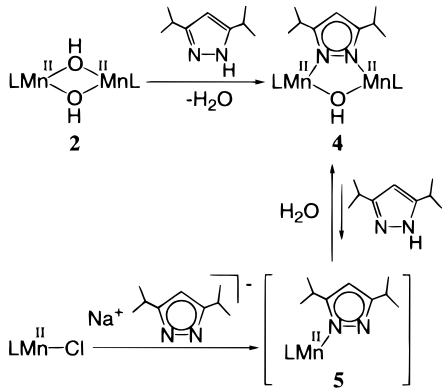
formula	$C_{70.5}H_{126}N_{14}OB_2Mn_2$
fw	1317.36
space group	triclinic
cryst system	$P\bar{1}$ (No. 2)
a/Å	14.944(5)
b/Å	22.142(6)
c/Å	3.263(5)
α/deg	97.48(3)
β/deg	101.85(3)
γ/deg	109.81(2)
V/Å^3	3944(5)
Z	2
D(calcd)/g·cm^{-1}	1.14
cryst size/mm	0.2 × 0.2 × 0.15
data collcn temp/°C	−60
diffractometer	Rigaku AFC-5S
radiation	graphite-monochromated Mo Kα (λ = 0.710 68 Å)
μ(Mo Kα)/cm^{-1}	3.67
scan mode	$\omega-2\theta$
scan width/deg	1.30 + 0.14 tan θ
scan speed/deg·min^{-1}	6
2θ range	3−45
octant measd	$\pm h,\pm k,+l$
no. of measd reflcns	10 848
no. of obsd reflcns	5610 ($I \geq 3\sigma(I)$)
no. of params refined	777
R/%	5.63
R_w/%	5.75

Results and Discussion

Characterization of the (μ-Hydroxo)(μ-pyrazolato)dimanganese(II) Complex 4. As we reported previously, a series of first-row transition metal hydroxo complexes $[Tp^{Pr^i_2}M(OH)]_n$ (M = Mn, Fe, Co, Ni, Cu, n = 2; M = Zn, n = 1) is basic enough to react with CO_2, esters, phosphate esters, amides, and various protic acids.[1a,6,8,10,11] Therefore the Mn(II) hydroxo complex **2** is expected to react with 3,5-diisopropylpyrazole to give Mn(II) pyrazolato species. In the reaction of **2** with 1 equiv of 3,5-Pr^i_2pzH (Mn:pyrazole = 2:1), one of the two hydroxide ligands of **2** was replaced by the pyrazolate to give an almost quantitative yield of a dinuclear (μ-hydroxo)(μ-pyrazolato)-dimanganese(II) complex, $Tp^{Pr^i_2}Mn(\mu\text{-}OH)(\mu\text{-}3,5\text{-}Pr^i_2pz)MnTp^{Pr^i_2}$ (**4**) (Scheme 2), the structure of which was confirmed by X-ray

(7) Kitajima, N.; Osawa, M.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 8952.
(8) Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5496.
(9) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.
(10) (a) Hikichi, S.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Chem. Soc., Chem. Commun.* **1992**, 814. (b) Hikichi, S.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Chem. Soc., Chem. Commun.* **1994**, 1737. (c) Kitajima, N.; Tamura, N.; Tanaka, M.; Moro-oka, Y. *Inorg. Chem.* **1992**, *31*, 3342. (d) Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737.
(11) Reaction of the dinuclear Mn(II) bis(μ-hydroxo) complex **2** with 1 equiv of CH_3COOH resulted in the formation of the Mn(II) μ-hydroxo μ-acetato complex, although X-ray crystallographical characterization of this complex has never been successful so far: (a) Kitajima, N.; Osawa, M.; Imai, S.; Fujisawa, K.; Moro-oka, Y.; Heerwegh, K.; Reed, C. A.; Boyd, P. D. W. *Inorg. Chem.* **1994**, *33*, 4613. (b) Osawa, M.; Fujisawa, K.; Kitajima, N.; Moro-oka, Y. *Chem. Lett.* **1997**, 919.

Scheme 2



crystallography (see below).[11] An IR spectrum of **4** contained a ν_{OH} band at 3685 cm^{-1}, which was distinct from that of the bis(μ-hydroxo) complex **2** (3712 cm^{-1}). Contrary to our expectation, reaction of **2** with 2 equiv of 3,5-Pr$^i_2$pzH (Mn: pyrazole = 1:1) also resulted in the isolation of **4** and the recovering of the unreacted pyrazole. In addition, the isolated **4** was relatively inert toward 3,5-Pr$^i_2$pzH. An IR spectrum of the reaction mixture of **4** with 5 equiv of 3,5-Pr$^i_2$pzH still contained the ν_{OH} band at 3685 cm^{-1} arising from **4**. In the formation of **4** from **2**, 3,5-Pr$^i_2$pzH behaved as acid to give the pyrazolate ligand, but its acidity might not be strong enough because of the electron-donating ability of the Pr^i substituents on the pyrazole ring. Remarkably, although a Mn(II) pyrazolato complex, Tp$^{Pr^i_2}$Mn(3,5-Pr$^i_2$pz) (**5**), could be prepared by anion exchange reaction of Tp$^{Pr^i_2}$MnCl and Na(3,5-Pr$^i_2$pz), its attempted purification resulted in isolation of the (μ-hydroxo)-(μ-pyrazolato)dimanganese(II) complex **4**. These observations imply that the pyrazolato complex **5** may be sterically unfavorable[12] and quite sensitive to moisture to give the hydrolyzed product **4**.

The molecular structure of **4** is represented in Figure 1, and pertinent structural parameters are summarized in Table 2. It has been known that pyrazolate anion can bind to metal centers as monodentate (=η^1),[13] bidentate (=η^2),[14] and bridging (=μ)[15] ligands, although η^2-pyrazolate ligands are found for lanthanide, actinide, and high-valent early transition metal complexes. The coordination geometries of two Mn centers in **4** are different; Mn1 has a distorted square-pyramidal geometry, and in contrast, the geometry of Mn2 is trigonal bipyramid with the N2−Mn2−N41 axis (170.2(2)°), where N1 serves as an equatorial ligand

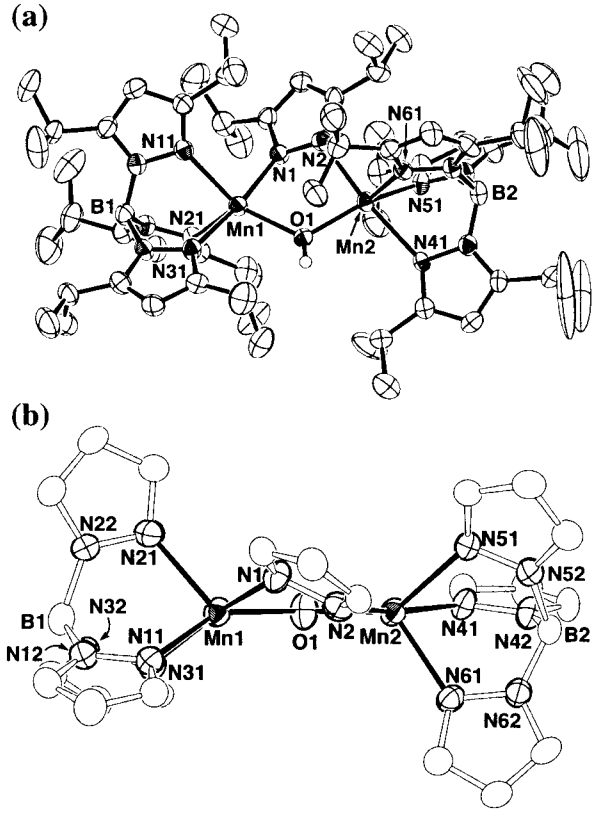


Figure 1. ORTEP diagram of **4**·1.5C_5H_{12} (drawn at the 50% probability level): (a) Whole molecule of **4**; (b) view of **4** looking down parallel to the Mn1−O1−Mn2 plane. All hydrogen atoms except that attached to the oxygen atom and in the pentane molecules are omitted for clarity. In b, all isopropyl substituent groups on the pyrazolyl rings are also omitted.

of the square pyramidal Mn1 center and N2 occupies the apical site of the trigonal bipyramid. Accordingly, the bond length of Mn2−N2 (2.215(6) Å) is longer than that of Mn1−N1 (2.160(5) Å). The relatively large torsion angle of Mn1−N1−N2−Mn2 (48.8(5)°) indicates distortion of the five-membered metallacyclic structure (Mn1−N1−N2−Mn2−O1). Steric hindrance due to the isopropyl groups of the Tp$^{Pr^i_2}$ ligands and the bridging 3,5-Pr$^i_2$pz ligand may be responsible for the asymmetric environments of the Mn centers and the distorted configuration of the bridging pyrazolate.

Reactivity of the (μ-hydroxo)(μ-pyrazolato)dimanganese-(II) Complex 4. We examined the reactivity of **4** toward H_2O_2 and O_2, because **4** was a possible precursor of the pyrazole-

(12) According to a theoretical study (see ref 14h), the presence of the empty d-orbitals on the metal strongly favors η^2-bonding because of the interaction between the nitrogen lone pairs and the d-orbitals. In Mn(II) ($S = {}^5/_2$) complexes, therefore, η^2-bonding pyrazolate may be unfavorable and the pyrazolato complex **5** is expected as a mononuclear η^1-pyrazolato or a dinuclear bis(μ-pyrazolato) complex.

(13) See for example: (a) Carmona, D.; Lahoz, F. J.; Oro, L. A.; Lamata, M. P.; Buzarra, S. *Organometallics* **1991**, *10*, 3123. (b) Minghetti, G.; Banditelli, G.; Bonati, F. *J. Chem. Soc., Dalton Trans.* **1979**, 1851.

(14) (a) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Hemling, H.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 874. (b) Deacon, G. B.; Gatehouse, B. M.; Nickel, S.; Platts, S. M. *Aust. J. Chem.* **1991**, *44*, 613. (c) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M. *Aust. J. Chem.* **1993**, *46*, 1881. (d) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Hemling, H.; Schumann, H. *Aust. J. Chem.* **1994**, *47*, 1223. (e) Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653. (f) Sun, Y.; McDonald, R.; Takats, J.; Day, V. W.; Eberspacher, T. A. *Inorg. Chem.* **1994**, *33*, 4433. (g) Röttger, D.; Erker, G.; Grehl, M.; Fröhlich, R. *Organometallics* **1994**, *13*, 3897. (h) Guzei, I. A.; Baboul, A. G.; Yap, G. P. A.; Rheingold, A. L.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1997**, *119*, 3387. (i) Guzei, I. A.; Yap, G. P. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 1738.

(15) (a) Coleman, A. W.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 922. (b) Marshall, J. L.; Hopkins, M. D.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1992**, *31*, 5034. (c) López, G.; Ruiz, J.; García, G.; Vicente, C.; Casabó, J.; Molins, E.; Miravitlles, C. *Inorg. Chem.* **1991**, *30*, 2605. (d) Jain, V. K.; Kannan, S.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3625. (e) Carmona, D.; Mendoza, A.; Ferrer, J.; Lahoz, F. J.; Oro, L. A. *J. Organomet. Chem.* **1992**, *431*, 87. (f) López, G.; Ruiz, J.; García, G.; Vicente, C.; Rodríguez, V.; Sánchez, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 1681. (g) López, G.; García, G.; Sánchez, G.; García, J.; Vegas, A.; Martínez-Ripoll, M. *Inorg. Chem.* **1992**, *31*, 1518. (h) Carmona, D.; Lamata, P. M.; Esteban, M.; Lahoz, F. J.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *J. Chem. Soc., Dalton Trans.* **1994**, 159. (i) Carmona, D.; Ferrer, J.; Mendoza, A.; Lahoz, F.; Reyes, J.; Oro, L. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1171. (j) Beveridge, K. A.; Bushnell, G. W.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J. *Organometallics* **1983**, *2*, 1447. (k) Carmona, D.; Oro, L. A.; Lamata, M. P.; Jimeno, M. L.; Elguero, J.; Belguise, A.; Lux, P. *Inorg. Chem.* **1994**, *33*, 2196. (l) Cámpora, J.; López, J. A.; Palma, P.; Ruíz, C.; Carmona, E. *Organometallics* **1997**, *16*, 2709.

Scheme 3

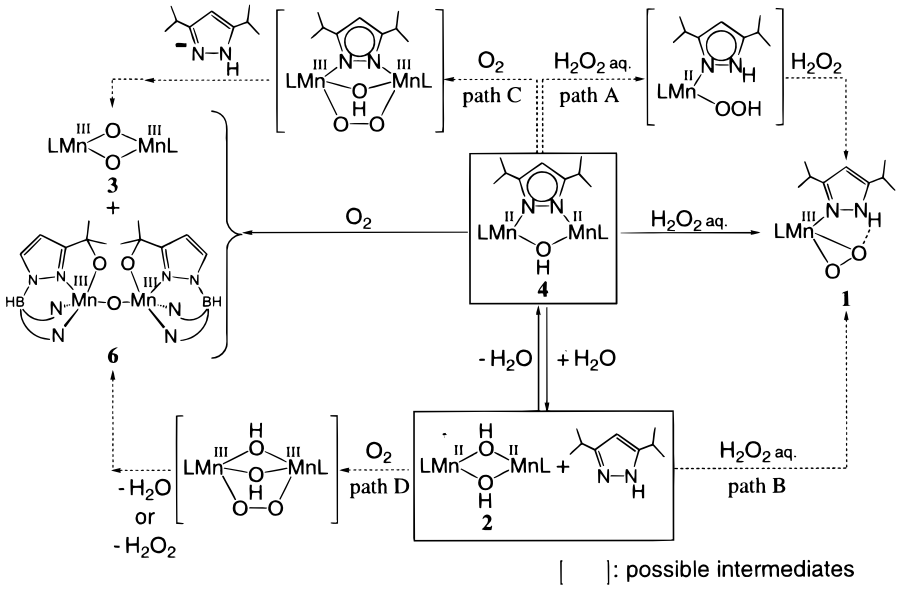


Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Tp^{Pr^i_2}Mn(\mu\text{-}OH)(\mu\text{-}3,5\text{-}Pr^i_2pz)MnTp^{Pr^i_2}\cdot 1.5C_5H_{12}$ ($\mathbf{4}\cdot 1.5C_5H_{12}$)

Interatomic Distances					
Mn1−O1	2.075(5)	M1−N1	2.160(5)	Mn1−N11	2.275(6)
Mn1−N21	2.178(6)	Mn1−N31	2.274(6)	Mn2−O1	2.047(5)
Mn2−N2	2.215(6)	Mn2−N41	2.350(6)	Mn2−N51	2.187(6)
Mn2−N61	2.182(6)	N1−N2	1.396(7)	Mn1···Mn2	3.603(2)

Bond Angles			
O1−Mn1−N1	84.6(2)	O1−Mn1−N11	149.7(2)
O1−Mn1−N21	116.4(2)	O1−Mn1−N31	99.5(2)
N1−Mn1−N11	89.6(2)	N1−Mn1−N21	104.8(2)
N1−Mn1−N31	169.1(2)	N11−Mn1−N21	93.9(2)
N11−Mn1−N31	81.8(2)	N21−Mn1−N31	82.5(2)
O1−Mn2−N2	86.1(2)	O1−Mn2−N41	101.0(2)
O1−Mn2−N51	141.1(2)	O1−Mn12−N61	124.0(2)
N2−Mn2−N41	170.2(2)	N2−Mn2−N51	104.8(2)
N2−Mn2−N61	99.7(2)	N41−Mn2−N51	79.5(2)
N41−Mn2−N61	82.1(2)	N51−Mn2−N61	94.8(2)

containing Mn(III) peroxo complex **1**. As expected, reaction of the (μ-hydroxo)(μ-pyrazolato)dimanganese(II) complex **4** with H_2O_2 yielded the peroxo complex **1′** (alternative structural isomer being in thermal equilibrium with the hydrogen-bonding peroxo complex **1**) without further addition of 3,5-Pr^i_2pzH. However, reaction of **4** with O_2 gave a mixture of products similar to that obtained from the bis(μ-hydroxo) complex **2** and O_2, i.e., the dinuclear Mn(III) bis(μ-oxo) complex **3** and the $Tp^{Pr^i_2}$-ligand-oxygenated Mn(III) μ-oxo complex {Mn[HB(3-OCMe$_2$-5-Pr^ipz)(3,5-Pr^i_2pz)$_2$]}$_2$(μ-O) (**6**).[7] In addition, formation of the mononuclear peroxo complex **1** (and **1′**) was never observed in the O_2 oxygenation reaction. This result led us to inspect the replacement reaction of the bridging pyrazolato ligand in **4**.

Treatment of a CH_2Cl_2 solution of **4** with H_2O afforded a mixture of the (μ-hydroxo)(μ-pyrazolato)dimanganese(II) complex **4** and the bis(μ-hydroxo) complex **2**. In addition, **4** was also obtained from the solution of the pyrazolato complex **5** (vide supra). The basicity of 3,5-$Pr^i_2pz^-$ is strong due to the electron-donating Pr^i substituents on the pyrazole ring; therefore, the pyrazolate ligand might be easily protonated and dissociate in the presence of H_2O. Steric repulsion between the hindered Pr^i groups of the $Tp^{Pr^i_2}$ and pyrazolate ligands is also expected to enhance the lability of the 3,5-$Pr^i_2pz^-$ ligands in **4** and **5**.

Plausible mechanisms of the oxygenation reactions are summarized in Scheme 3. The mononuclear peroxo−pyrazole complex **1** was formed by the reaction of the (μ-hydroxo)(μ-pyrazolato)dimanganese(II) complex **4** with *aqueous* H_2O_2. Therefore, the pyrazolate ligand is easily hydrolyzed to cleave the dimeric structure, and a mononuclear intermediate containing the resulting pyrazole ligand is formed (path A). However, we cannot rule out the possibility that the dinuclear bis(μ-hydroxo) complex **2** reacts with H_2O_2, and the neutral pyrazole works as a strong σ-donating aromatic N ligand to stabilize the resultant mononuclear 6-coordinate octahedral Mn(III) center (path B).

In reductive O_2 activation, it is known that electrochemical reduction potential of dioxygen to peroxide in a two-electron-transfer step is less positive than that of the one-electron reduction (i.e. dioxygen to superoxide), and the bimetallic reaction centers may be advantageous for the two-electron reduction giving μ-peroxo species. In the oxygenation reaction by O_2, therefore, dinuclear Mn(III)−μ-peroxo intermediates would be involved. Two possible reaction pathways are presented in Scheme 3; direct reaction of **4** and O_2 yields a corresponding μ-peroxo intermediate (path C), or the hydroxo complex **2**, which is produced by contaminated moisture in O_2 gas or solvent, reacts with O_2 (path D). Thus, formation of **3** and **6** proceeds via dissociation of pyrazole (path C) and H_2O (path D) followed by O−O bond rupture of peroxide and/or elimination of peroxide as H_2O_2 from the μ-peroxo−bis(μ-hydroxo) intermediate (path D). It is notable that the mononuclear peroxo complex **1** is never yielded by O_2 oxygenation. This result implies that disproportionation of the dinuclear Mn(III) μ-peroxo intermediates is not involved in the process of the formation of **1**, and excess amount of H_2O_2 may work as oxidant toward the metal center.

In conclusion, the (μ-hydroxo)(μ-pyrazolato)dimanganese(II) complex **4** has been successfully isolated and characterized. In the presence of H_2O, the pyrazolate ligand is readily hydrolyzed to regenerate the bis(μ-hydroxo) complex **2**. Oxygenation of **4** by H_2O_2 affords the mononuclear Mn(III) peroxo pyrazole

complex **1**, although the detailed reaction mechanism remains to be studied.[16] To reveal the role of the pyrazole ligand, investigation of the reaction of the hydroxo complex with H_2O_2 in the presence of various σ-donating ligands is under study.

(16) We have been trying to characterize the solution-state structures of the pyrazololato complexes (**4** and **5**) and the reaction intermediates, although our attempts have not been successful so far because of the high reactivity and instability of the Mn(II) complexes toward O_2 and the complicating features of their solution IR spectra in the presence of H_2O and/or pyrazole.

Acknowledgment. We are grateful to the Ministry of Education, Science, Sports, and Culture of the Japanese government for financial support of the research (Grant-in-Aid for Specially Promoted Scientific Research No. 08102006).

Supporting Information Available: Atomic numbering schemes and tables of positional parameters, thermal parameters, and bond lengths and angles for **4**·1.5C_5H_{12} (11 pages). Ordering information is given on any current masthead page.

IC971622X