

and the asymmetric variant of the metal-catalyzed carbomagnesation are in progress.

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Supplementary Material Available: Experimental procedures and spectral and analytical data for all reaction products (17 pages). Ordering information is given on any current masthead page.

A Novel Dioxygenase Type Oxygen Insertion. CH Bond Oxidation of Isopropyl Groups in a Dimanganese Complex with Molecular Oxygen

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Activation of molecular oxygen by transition-metal complexes has attracted much attention in recent years.¹ In the present communication, we report a novel dioxygenase type ligand oxidation in a dimanganese complex with molecular oxygen; both atoms of dioxygen molecule are incorporated into the CH bonds of isopropyl groups in the complex.

Recently, we have reported the oxidative conversion of a (di- μ -hydroxo)manganese(II,II) complex $[\text{Mn}(\text{HB}(3,5\text{-iPr}_2\text{pz})_3)_2(\text{OH})_2]$ (**1**) to the corresponding (di- μ -oxo)manganese(III,III) complex **2**.² The conversion proceeds almost quantitatively by anaerobic oxidation of **1** with KMnO_4 . However, when **1** was aerobically oxidized, noted was formation of another product **3**, besides **2**. Thus, when **1** was stirred in toluene at room temperature under 1 atm of O_2 for 30 min, both **2** and **3** were obtained with yields (based on **1**) of 51 and 38%, respectively.³ Each product was isolated by careful fractional recrystallizations from MeCN. Complex **3** is colored in deep blue and is clearly distinct from **2**, which is deep brown. Figure 1 represents the molecular structure of **3** determined by X-ray crystallography.⁴ Complex **3** has a dinuclear structure in which the two manganese ions are solely bridged with an oxo ligand. The unusual structural feature of the complex is that one isopropyl group in each tris-(pyrazolyl)borate ligand is oxygenated and it coordinates to each manganese ion as an alkoxo ligand. The complex is neutral; therefore, the valence of the manganese is ascribed to Mn(III).

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(3) IR $\nu(\text{BH})$ 2525 cm^{-1} ; UV-vis (toluene) 399 (sh), 467 (ϵ , 286), 625 nm (707); $^1\text{H NMR}$ (toluene- d_6 , -40°C , δ , ppm) 0.98 (br, 12 H, Me_2CO), 1.42 (br, 24 H, Me_2CH), 1.67 (br, 36 H, Me_2CH and Me_2CO), 4.95 (br, 10 H, Me_2CH), 8.14 (br, 2 H, pz), 11.42 (br, 4 H, pz); FD-MS (m/e) 1086. Anal. Calcd for $\text{C}_{54}\text{H}_{90}\text{N}_{12}\text{O}_3\text{B}_2\text{Mn}_2$: C, 59.62; H, 8.28; N, 15.53. Found: C, 59.88; H, 8.41; N, 15.43.

(4) **3** (MW 1086.66) crystallized in the monoclinic space group P_21/n with $a = 16.230$ (7) \AA , $b = 18.271$ (7) \AA , $c = 24.925$ (10) \AA , $\beta = 106.70$ (3)°, $V = 7079.5$ (5) \AA^3 , $Z = 4$, $D_c = 1.020$, $D_m = 1.02 \pm 0.01$ g cm^{-3} . Data collection ($6^\circ \leq 2\theta \leq 45^\circ$) was completed on a Rigaku AFC-5R diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation. The structure was solved by the direct method (TEXSAN) and refined by a block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were calculated and fixed in the final refinements. The refinement currently converged at the $R(R_w)$ factor of 9.3 (12.7)% for 4026 reflections ($F_o \geq 3\sigma(F_o)$).

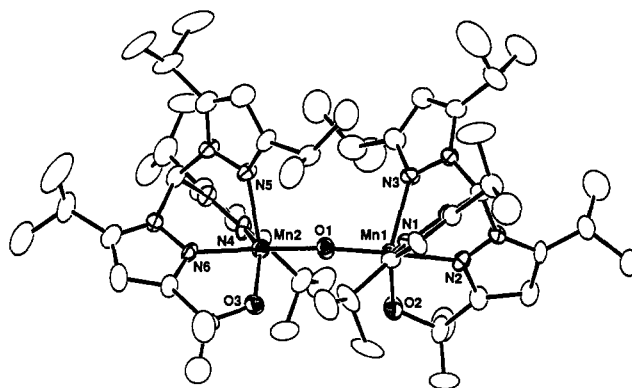


Figure 1. ORTEP drawing of **3**. Selected bond distances (\AA) and angles (deg) are as follows: Mn1-N1, 2.19 (1); Mn1-N2, 1.97 (1); Mn1-N3, 2.19 (1); Mn1-O1, 1.77 (1); Mn1-O2, 1.88 (1); Mn2-N4, 2.14 (1); Mn2-N5, 2.18 (1); Mn2-N6, 1.95 (1); Mn2-O1, 1.77 (1); Mn2-O3, 1.89 (1); Mn1...Mn2, 3.530 (4); Mn-O1-Mn2, 174.9 (7).

As consistent with the structure, the FD-MS spectrum of **3** exhibits a peak at 1086 due to the molecular ion. Another notable feature of **3** is that it gives rise to a reasonably sharp and isotropically shifted $^1\text{H NMR}$ spectrum. The low magnetic susceptibility (2.88 $\mu\text{B/mol}$ at 296 K) also suggests the strongly antiferromagnetic property of **3**.

When **1** was oxidized with dioxygen in the presence of 10 equiv of PPh_3 , the formation of **3** was completely ceased, whereas **2** was obtained with the same yield (ca. 50%) as in the absence of PPh_3 . In this reaction, OPPh_3 was formed in 84% yield based on **1**.

In order to ascertain the origin of the three oxygen atoms in **3**, labeling experiments were performed by FD-MS spectroscopy. When ^{18}O labeled **1** was oxidized with $^{16}\text{O}_2$, only one ^{18}O atom was incorporated into **3**, while two ^{18}O atoms were incorporated when **1** containing ^{16}O was treated with $^{18}\text{O}_2$. These results clearly indicate that the μ -oxo atom in **3** is originated from the hydroxo groups in **1**, and both alkoxo oxygen atoms come from the molecular oxygen. In these experiments, the formed di- μ -oxo complex **2** was also analyzed, establishing that both oxo ligands come from the hydroxo groups in **1**. When **1** containing ^{16}O was oxidized with a 1:1 mixture of $^{16}\text{O}_2$ and $^{18}\text{O}_2$, produced was **3** labeled with $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ with comparable yields; **3** containing $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ was not formed considerably. Therefore, it is conclusive that the two alkoxo oxygen atoms in **3** are originated from the same dioxygen molecule.

On the basis of these experimental results, we propose the following reaction mechanism. The initial reaction between the five-coordinate dimanganese(II) complex (**1**) and molecular oxygen is ascribed to formation of a (μ -peroxo)dimanganese(III) complex (**4**) which retains the di- μ -hydroxo core. Dissociation of H_2O_2 (the origin is the peroxide ion) from **4** affords **2**. As a competitive reaction, dissociation of H_2O does occur, generating a μ -oxo- μ -peroxo intermediate (**5**). Complex **5** undergoes homolysis of the O-O bond to give a dinuclear Mn(IV) oxo intermediate (**6**), which is responsible for the ligand oxidation.⁵⁻⁹ The oxo intermediate **6** oxygenates PPh_3 to OPPh_3 much faster than the isopropyl CH bond; therefore, PPh_3 works as an inhibitor for the formation of **3**. As consistent with the mechanism, the oxygenated isopropyl groups in **3** assume a cis configuration. Thus,

(5) Homolysis of O-O bond of the peroxide ion in dinuclear μ -peroxo complexes is established for Fe and Cu.^{6,7} The reaction of a Ru(II) porphyrin complex with molecular oxygen results in formation of a Ru(IV)-oxo complex which is effective for epoxidation of olefins.⁸

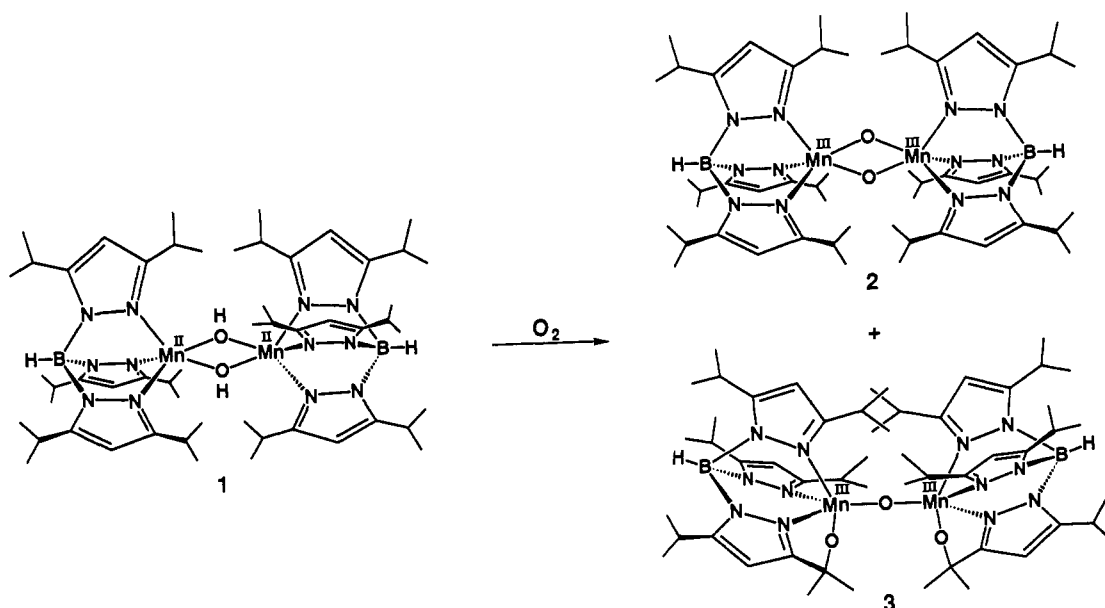
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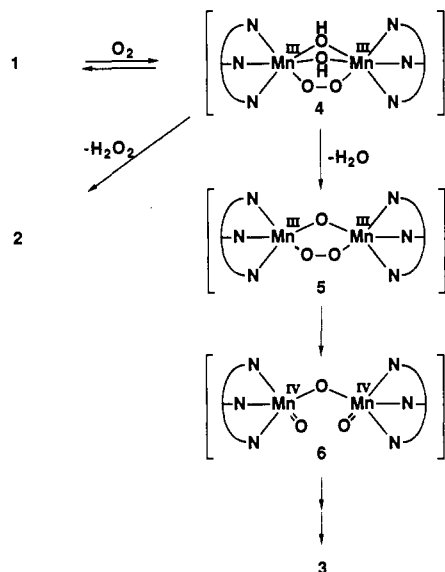
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Scheme I



Scheme II



the appropriate orientation and proximity of the isopropyl groups to the reactive oxo ligands in **6** is also an important factor for the present intramolecular reaction.

A few examples of aerobic ligand oxidations of transition-metal complexes have previously been reported. These include the oxidations of aromatic rings in dinuclear Cu complexes,¹⁰ olefinic ligand oxidation in an Ir complex,¹¹ and aliphatic CH bond oxidation in a Ni complex.¹²

The present ligand oxidation may provide us with a useful method to prepare a new type tris(pyrazolyl)borate ligand containing a functional group on one pyrazole ring. Thus, currently,

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efforts are being made to remove the manganese ions from **3**.

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Supplementary Material Available: Tables of crystal data, atomic coordinates with isotropic thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles (17 pages); listing of observed and calculated structure factors (28 pages). Ordering information is given in any current masthead page.

$(\eta^2-C_{70})Ir(CO)Cl(PPh_3)_2$: The Synthesis and Structure of an Organometallic Derivative of a Higher Fullerene

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The availability of macroscopic quantities of C_{60}^{1-4} has rapidly led to remarkable discoveries of its chemical (formation of crystalline, structurally characterized transition-metal complexes,⁵⁻⁷ hydrogenation,⁴ fluorination⁸) and physical (metallic conductivity,^{10,11} superconductivity^{12,13} and soft ferromagnetism¹³ in

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