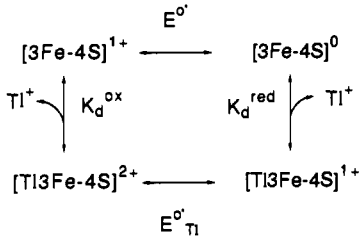
Scheme I



Tl^+ effectively stabilizes the "0" level. Coordination of Tl^+ to the oxidized cluster is weak, but nevertheless represents the first reported interaction of a metal ion other than Fe^{2+} with the less electron rich $[3Fe\text{-}4S]^{1+}$ species.[16] In the amino acid sequence that forms the binding domain for the [3Fe-4S] cluster, a cysteine that would normally provide[17] the fourth ligand for [4Fe-4S] centers is replaced by aspartate.[3,18] Thus carboxylate and/or H_2O (OH^-) are likely noncluster ligand(s) to thallium.[15]

Because of the similarity of Tl^+ and K^+ in charge and size, Tl^+ has been used to probe K^+ binding sites in enzymes[19] and ion channels.[20] Here, a different type of interaction is evident, one showing the preference of Tl^+ for polarizable ligands. The affinity of Tl^+ for $[3Fe\text{-}4S]^0$ is much higher than values reported for K^+ binding sites (for which K_d is typically in the millimolar range[19]) and implicates the cluster as a possible biological target for this toxic element.[21] There is an interesting similarity with the crown thioether complex $[Tl([9]aneS_3)]^{1+}$ in which Tl(I) is coordinated facially with an average Tl-S distance of 3.1 Å.[22] The [3Fe-4S] core also provides a tripodal S donor system, but one for which the propensity for metal ion coordination can be modulated by the core oxidation level. Observation of near-ideal wave shapes[23] throughout the concentration range 10^{-5}–0.5 M Tl^+ at scan rates up to 470 mV s^{-1} shows that Tl^+ "on" and "off" rates are fast. Thus the metal binding site at [3Fe-4S] in Fd III is probably exposed to solvent, and the protein offers little resistance to the transformation. Because of the possibility of interference with normal biochemical function, it is of interest to determine how general this reactivity is.

Acknowledgment. This work was supported by the University of California, by grants from NATO (CRG 900302) and from the Molecular Recognition Initiative of the SERC of the UK, and by an Exxon Education Foundation Award (F.A.A.).

(16) The core cluster $[4Fe\text{-}4S]^{3+}$, which represents the product of the reaction between Fe^{2+} and the oxidized cluster $[3Fe\text{-}4S]^{1+}$, is known in proteins called high-potential iron proteins, HiPIP (Carter, C. W., Jr.; Kraut, J.; Freer, S. T.; Alden, R. A. *J. Biol. Chem.* **1974**, *249*, 6339) and also a synthetic model compound $[Fe_4S_4(S\text{-}2,4,6\text{-}(i\text{-}Pr)_3C_6H_2)_4](Bu_4N)$ (O'Sullivan, T.; Millar, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 4096).

(17) Fukuyama, K.; Nagahara, Y.; Tsukihara, T.; Katsube, Y.; Hase, T.; Matsubara, H. *J. Mol. Biol.* **1988**, *199*, 183. Otaka, E.; Ooi, T. *J. Mol. Evol.* **1987**, *26*, 257.

(18) Bovier-Lapierre, G.; Bruschi, M.; Bonicel, J.; Hatchikian, E. C. *Biochim. Biophys. Acta* **1987**, *913*, 20.

(19) Kayne, F. J. *Arch. Biochem. Biophys.* **1971**, *143*, 232. Markham, G. D.; Hafner, E. W.; Tabor, C. W.; Tabor, H. *J. Biol. Chem.* **1980**, *255*, 9082. Bostain, K. A.; Betts, G. F.; Man, W. K.; Hughes, M. N. *Biochem. J.* **1982**, *207*, 73. Markham, G. D.; Leyh, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 599. Lord, K. A.; Reed, G. H. *Inorg. Chem.* **1987**, *26*, 1464.

(20) Miller, I. R. *Biochim. Biophys. Acta* **1985**, *817*, 199. Nelson, A. *J. Electroanal. Chem.* **1991**, *303*, 221.

(21) Douglas, K. T.; Bunni, M. A.; Baindur, S. R. *Int. J. Biochem.* **1990**, *22*, 429.

(22) Blake, A. J.; Greig, J. A.; Schroeder, M. *J. Chem. Soc., Dalton Trans.* **1991**, 529.

(23) Half-height widths were 100–105 mV; see: Laviron, E. *J. Electroanal. Chem.* **1974**, *52*, 355, 395. At Tl^+ concentrations below 5 μM, we observed that the voltammetric signals became distorted by asymmetric broadening. The reason for this is unclear but may be a combination of $[Tl^+]$ levels being lower than needed for saturation of the binding sites, combined with the decreased "on" rate. The effect could be decreased by use of a rotating disk electrode (minimizing mass transport limitations) and by use of slow scan rates. Even so, voltammograms for this low concentration region were not included in the data analysis and were unnecessary because of the high confidence in $E^{\circ\prime}([Tl]^+ = 0)$. Further investigations of this phenomenon are under way.

Stereoselective Zirconium-Catalyzed Ethylmagnesation of Homoallylic Alcohols and Ethers. The Influence of Internal Lewis Bases on Substrate Reactivity

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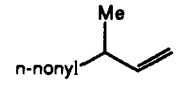
We recently reported a zirconium-catalyzed carbomagnesation that effects the stereoselective addition of EtMgCl to unactivated alkenes.[1] Reactions of allylic alcohols and ethers proceed with a complementary sense of stereoinduction. The reversal of stereoselectivity was attributed to the association of the magnesium alkoxide (and not ethers) with the zirconium reagent. Herein we report on the ethylmagnesation of acyclic and cyclic homoallylic alcohols and ethers.

As is illustrated in Table I, treatment of the anti homoallylic alcohol **1a** with 4 equiv of EtMgCl and 5 mol % Cp_2ZrCl_2 in Et_2O (25 °C, 12 h), followed by the addition of $B(OMe)_3/H_2O_2$ (−78 °C), provides **2a** in 75% isolated yield with ≥99:1 selectivity.[2] Ethylmagnesations of **1b** and **1c** proceed with the same sense of stereoinduction as is observed with **1a**. Several conclusions can be derived from the study of the carbometalations of **1a–c**: (1) Binding from the homoallylic position is more effective than from the allylic site. The adverse influence of THF on the stereochemical outcome of the reactions of homoallylic metal alkoxides is less pronounced than on that of the allylic systems.[1] The uniform sense of stereoinduction in reactions of **1a–c** implies that, in contrast to allylic ethers, homoallylic ethers may bind to the transition metal and direct the course of the reaction. (2) Internal chelation leads to selectivity. With a more effective internal Lewis base, higher stereoselectivities are observed (see **1a** and **1c**); THF does not compete with a strong ligating group, but alters the binding of less efficient internal ligands (OMEM, **1c**) to inflict a diminution in stereocontrol. Without internal coordination, no stereoselectivity can be achieved: ethylmagnesation of **4** provides a 1:1 diastereomeric mixture of products. (3) Heteroatom–metal coordination leads to enhanced reactivity. When such coordination is altered, either because of an inferior Lewis base (compare **1a** and **1c**, Table I) or due to the presence of a competing ligating solvent (THF), reaction efficiency is seriously reduced. With both an inferior Lewis base and a coordinating solvent, no reaction is observed (**1c** in THF, Table I). In accord with this trend, whereas carbometalation of **1a** occurs in 75% yield, that of **4** proceeds to only 15% conversion (90% mass balance).



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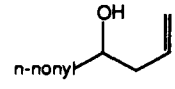

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Ethylmagnesation of syn homoallylic alcohol **5a** (Table II) proceeds less efficiently and selectively (55%, 85:15) than that of the corresponding anti isomer **1a** (75%, ≥99:1). Unlike the

(1) Hoveyda, A. H.; Xu, Z. *J. Am. Chem. Soc.* **1991**, *113*, 5079–5080. For related studies, see: (a) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266–6268. (b) Knight, K. S.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6268–6270.

(2) All compounds reported herein gave ^1H NMR, ^{13}C NMR, IR, and combustion analysis data consistent with the structure given. The stereochemical identity of **2a** was determined through decoupling and NOE experiments on the derived lactone I (Pt/O_2); enhancements were observed between H_2 and H_3, and H_1 and H_2, and none was observed between H_1 and H_3. Reaction of I with DBU/MeOH led to the formation of the all-equatorial, anti,anti isomer (100%); further supporting NMR studies were performed on the latter compound. See the supplementary materials for details.

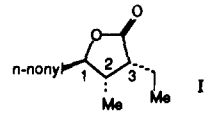

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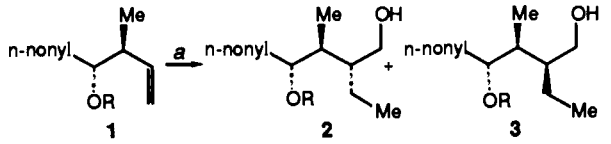
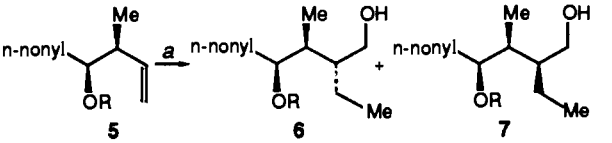
Table I. Diastereochemical Control in the Ethylmagnesation of Anti Homoallylic Alcohols and Derivatives



substrate	R	solvent	anti:syn (2:3)[b]	yield,[c] %
1a	H	Et_2O	>99:1	75
		THF	99:1	75
1b	Me	Et_2O	97:3	65
		50% Et_2O/THF	97:3	35
		THF	-	5
1c	MEM	Et_2O	92:8	50
		50% Et_2O/THF	87:13	26
		THF	-	0

[a] Conditions: 3–4 equiv of EtMgCl, 5 mol % Cp_2ZrCl_2, 12 h; B-(OMe)$_3$; H_2O_2. [b] Ratios determined by GLC analysis of lactones. [c] Isolated yields of purified products; mass balance ≥95% in all reactions.

Table II. Diastereochemical Control in the Ethylmagnesation of Syn Homoallylic Alcohols and Derivatives



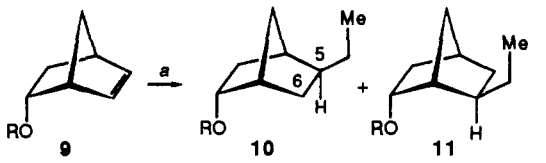
substrate	R	solvent	anti:syn (6:7)[b]	yield,[c] %
5a	H	Et_2O	85:15	55
		THF	84:16	55
5b	Me	Et_2O	65:35	38
		THF	50:50	5
5c	MEM	Et_2O	50:50	33
		THF	-	0

[a] Conditions: 3–4 equiv of EtMgCl, 5 mol % Cp_2ZrCl_2, 12 h; B-(OMe)$_3$, H_2O_2. [b] Ratios determined by GLC analysis of lactones. [c] Isolated yields of purified products. Mass balance ≥95% in all reactions.

anti derivatives, ethers **5b** and **5c** are carbometalated with poor diastereoselectivity. Thus, the level of stereoinduction is dependent upon local chirality.[3] Presumably, molecular organization, arising from substrate–catalyst binding, leads to unfavorable torsional interactions in the syn but not the anti series (vide infra); binding may thus be weaker and less π-facial selective in reactions of **5a–c** (especially with Me and MEM ethers), leading to lower yields and selectivities. The data in Tables I and II show that the stereogenic center α to the olefin is the principal stereodifferentiating element, as the newly generated C–C bond is uniformly anti to this functionality. Accordingly, carbomagnesation of **8** is found to be nonselective (75%, 1:1).

Zirconium-catalyzed carbomagnesations of disubstituted alkenes with alkylmagnesium halides are sluggish: carbometalation of norbornene provides a 35% yield of the desired product after 48 h.[4] Ethylmagnesation of *exo*-5-norbornen-2-ol is also low yielding; an equal mixture of exo alkyl regioisomers is formed in 35% total yield. In contrast, *endo*-5-norbornen-2-ol (**9a**) affords **10a** in 97% yield and >99:1 regioselectivity (Table III).[5] The data in Table III support the contention that the better the coordinating ability of the heteroatom (OMgCl > OMEM), the higher the reaction selectivity and efficiency.

Table III. Regiochemical Control in Ethylmagnesation of **9**



substrate	R	solvent	ratio (10:11)[b]	yield,[c] %
9a	H	Et_2O	>99:1	97
		THF	97:3	85
9b	MEM	Et_2O	97:3	75
		THF	80:20	45[c]

[a] Conditions: 3 equiv of EtMgCl, 5 mol % Cp_2ZrCl_2, 48 h; 10% HCl at −40 °C. [b] Ratios determined by GLC analysis of the acetates; ca. 3% (total) of endo isomers were formed in all reactions. [c] Thirty percent starting material was recovered.

With **9a**, the simultaneous association of the zirconium metal with the alkene[6] (to form the zirconacyclopropane) and the neighboring heteroatom[7] may culminate in the significant enhancement of reaction efficiency. Since C–C bond formation occurs from the exo face, it follows that the alkyl adduct may arise from an anti mode of addition (anti to the Zr–alkene complex).[8] In a nucleophilic attack on a metal–alkene system, based on the mechanistic postulates of Hoffmann,[9] the *reactive* metal–olefin complex is one where the metal has shifted toward a terminus of the double bond. It is tenable that, in reactions of **9a** and **9b**, the heteroatom binds (with varying degrees of efficiency) to the transition metal and directs its slippage toward C6, so that alkylation occurs regioselectively at the more distal carbon, C5. This mechanism scheme, as well as whether such a mode of addition pertains to reactions of acyclic substrates, is under investigation.[10]

In summary, in zirconium-catalyzed ethylmagnesations, coordination of a heteroatom with the transition metal is required for obtention of high stereoselectivity. Such association improves the efficiency of the carbometalation to a large extent; in the absence of a resident Lewis base, there may be little or no reaction. Studies in connection with the mechanism, synthetic applications,

(3) Such dependence of stereoselectivity on local chirality is characteristic of reactions which involve two-point association of the catalyst, or the reagent, with the substrate. For example, see: Mihelich, E. D.; Daniels, K.; Eikhoff, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 7690–7692.

(4) Dzhemilev, U. M.; Vostrikova, O. S.; Sultanov, R. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 1430–1433.

(5) For Ti-mediated addition of MeLi to **9**, see: Moret, E.; Schlosser, M. *Tetrahedron Lett.* **1985**, *26*, 4423–4426.

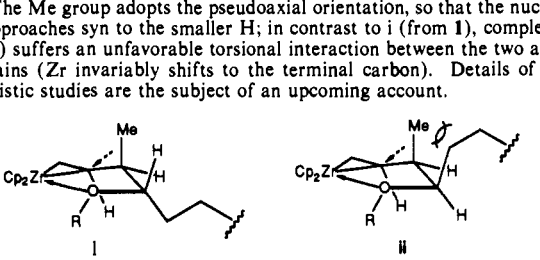
(6) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544–2546. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336–3346. (c) Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1989**, *111*, 4495–4496. (d) Nugent, W. A.; Taber, D. *J. Am. Chem. Soc.* **1989**, *111*, 6435–6437. (e) Takahashi, T.; Nitto, Y.; Seki, T.; Saburi, M.; Negishi, E. *Chem. Lett.* **1990**, 2259–2262.

(7) A notable aspect of the projected metal–alkene coordination is that it would require the involvement of the higher energy $2a_1$ orbital of the bound metal. See: Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 394–398.

(8) When the reaction is quenched with D_2SO_4, ^2H and ^{13}C NMR spectra show the incorporation of only one deuterium atom (at C6). Treatment with B(OMe)$_3$/H_2O_2 affords the exo alcohol exclusively. This outcome may have no bearing on the stereochemical identity of the initial metal–alkyl. Although studies with selected electrophiles indicate that Grignard reagents are trapped with retention (Jensen, F. R.; Nakamaye, K. L. *J. Am. Chem. Soc.* **1966**, *88*, 3437–3438), this can be dependent on the electrophile; in carbomagnesation of **9a**, quenching with O_2 affords 35% of the endo alcohol. Moreover, the Zr–Mg exchange could also proceed with inversion, as, for example, Ti–Li exchange can occur in such a manner; see: Hoppe, D.; Kramer, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 160–161.

(9) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320 and references cited therein. See also: Fujimoto, H.; Koga, N. *Tetrahedron Lett.* **1982**, *23*, 4357–4360.

(10) If we assume that anti addition pertains to reactions of acyclic substrates, transition-state models i and ii consistently account for our observations. The Me group adopts the pseudoaxial orientation, so that the nucleophile approaches syn to the smaller H; in contrast to i (from **1**), complex ii (from **5**) suffers an unfavorable torsional interaction between the two alkyl side chains (Zr invariably shifts to the terminal carbon). Details of our mechanistic studies are the subject of an upcoming account.



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

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Further assistance was provided by Boston College through a research incentive grant.

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 $[Mn(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)_2$ (**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 atom 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).

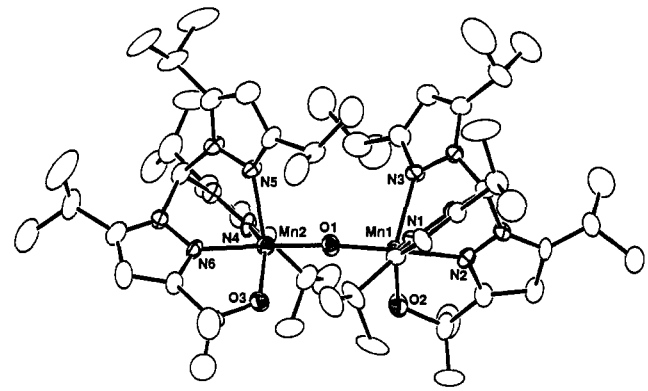

Figure 1. ORTEP drawing of **3**. Selected bond distances (Å) and angles (deg) are as follows: Mn1-N1, 2.19 (1); Mn1-N2, 1.97 (1); Mn1-N3, 2.19 (1); Mn1-O1, 1.77 (1); Mn1-O2, 1.88 (1); Mn2-N4, 2.14 (1); Mn2-N5, 2.18 (1); Mn2-N6, 1.95 (1); Mn2-O1, 1.77 (1); Mn2-O3, 1.89 (1); Mn1···Mn2, 3.530 (4); Mn-O1-Mn2, 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 ^1H NMR spectrum. The low magnetic susceptibility (2.88 μB/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 $^{16}O_2$, only one ^{18}O atom was incorporated into **3**, while two ^{18}O atoms were incorporated when **1** containing ^{16}O was treated with $^{18}O_2$. 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 $^{16}O_2$ and $^{18}O_2$, produced was **3** labeled with $^{16}O^{16}O^{16}O$ and $^{16}O^{18}O^{18}O$ with comparable yields; **3** containing $^{16}O^{16}O^{18}O$ 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,

(1) (a) Sheldon, R. A.; Kochi, J. A. *Metal-Catalyzed Oxidations of Organic Compounds*: Academic Press: New York, 1981. (b) *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E.; Sawyer, D. T., Eds.; Plenum Press: New York, 1988.

(2) Kitajima, N.; Udai, P. S.; Amagai, N.; Osawa, M.; Moro-oka, Y. *J. Am. Chem. Soc.* In press.

(3) IR ν(BH) 2525 cm^{-1}; UV-vis (toluene) 399 (sh), 467 (ϵ, 286), 625 nm (707); ^1H NMR (toluene-d_8, -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 $C_{54}H_{90}N_{12}O_3B_2Mn_2$: 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 $P2_1/n$ with a = 16.230 (7) Å, b = 18.271 (7) Å, c = 24.925 (10) Å, β = 106.70 (3)°, V = 7079.5 (5) Å^3, Z = 4, D_c = 1.020, D_m = 1.02 ± 0.01 g cm^{-3}. Data collection ($6° \le 2\theta \le 45°$) was completed on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo Kα 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 ($F_o \ge 3\sigma(F_o)$).

(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]

(6) Balch, A. L.; Chan, Y.-W., Cheng, R.-J.; La mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779.

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