

Electronic Supplementary Information

**Epoxidation of Alkenes and Oxidation of Alcohols with Hydrogen
Peroxide Catalyzed by a Manganese(V) Nitrido Complex**

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1. Materials

All chemicals were of reagent grade unless otherwise specified. $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ was synthesized according to a published procedure.¹ The purity of the complex was determined by CHN elemental analysis and UV/vis spectrophotometry. Alkenes were purified by passing through a short column of neutral alumina prior to use. Acetic acid and acetonitrile were purified according to standard methods.² Hydrogen peroxide (35% Riedel-de Haën) was used as received and standardized by iodometry.^{3,4} 2-Methyl-1-phenyl-2-propyl hydroperoxide (MPPH) was prepared according to a literature method,⁵ and its purity was determined to be >99% by NMR. Active MPPH levels were further measured by iodometric titrations, which showed >99% peroxide activity.

2. Instrumentation

Gas chromatographic analyses were performed on a HP5890 GC/FID equipped with a HP-5MS (30 m \times 0.25 mm i.d.) or a DB-FFAP (30 mm \times 0.25 mm i.d.) column. GC/MS measurements were carried out on a HP6890 gas chromatograph interfaced to a HP 5975 mass selective detector. Elemental analyses were done on an Elementar Vario EL analyzer. Electrospray ionization mass spectrometry (ESI/MS) was performed on a PE SCIEX API 365 mass spectrometer.

3. Catalytic oxidation

All experiments were carried out under argon atmosphere, unless otherwise specified.

General procedure for catalytic Oxidation of Alkenes and Alcohols with H₂O₂

H₂O₂ was added into a pink solution of (PPh₄)₂[Mn(N)(CN)₄] (0.01 mmol) in CH₃CN (1 mL) containing substrate (1 mmol) and acetic acid (0-1 mmol) at 23°C. The mixture was vigorously stirred for 10 min – 16 h. Chlorobenzene was then added as an internal standard, and the mixture was analyzed by GC and GC-MS.

Kinetic isotope effects for benzyl alcohol oxidation

Kinetic isotope effects were investigated by using an equimolar mixture of benzyl alcohol and *d*₇-benzyl alcohol as substrate. The organic products were quantified and identified by GC and GC-MS. The KIE value was obtained by taking the ratio of the corresponding areas from GC measurements.

4. Computational Study

The reaction mechanism for the tetracyano-nitrido manganate complex MnN(CN)₄²⁻ catalyzed epoxidation of ethene with hydrogen peroxide in the presence of acetic acid has been theoretically studied by density functional theory. The structures and energies of all molecular species are calculated at the B3LYP level⁶ with the LanL2DZ basis set⁷ for transition metal (Mn) and 6-311++G(d,p) basis set for the nonmetal atoms. The polarizable continuum model (PCM)⁸ is used to account for the solvent effects in acetonitrile. All calculations are performed with Gaussian 03 package of program.⁹

Table S1: Relative energetics (in kcal/mol) of epoxidation of ethene by tetracyanonitrido manganese complex with hydrogen peroxide and acetic acid at gas phase and in acetonitrile.

	Gas phase		Acetonitrile (PCM)	
	ΔH_{298}°	ΔG_{298}°	ΔH_{298}°	ΔG_{298}°
$\text{MnN}(\text{CN})_4^{2-} + \text{H}_2\text{O}_2 + \text{CH}_2\text{CH}_2 + 2\text{CH}_3\text{COOH}$	3.2	-17.3	-8.8	-29.3
$\text{INT1} + \text{CH}_2\text{CH}_2 + \text{CH}_3\text{COOH}$	0.0	0.0	0.0	0.0
$\text{INT2} + \text{CH}_2\text{CH}_2$	-17.3	-6.6	-9.8	1.3
$\text{TS1} + \text{CH}_2\text{CH}_2$	10.3	22.1	12.9	24.2
$\text{INT3} + \text{CH}_2\text{CH}_2$	6.7	19.2	10.5	21.2
TS2	25.0	47.1	32.8	54.3
$\text{INT4} + \text{CH}_2\text{CH}_2\text{O}$	-61.4	-51.3	-58.3	-47.4
$\text{INT5} + \text{CH}_2\text{CH}_2\text{O} + \text{CH}_3\text{COOH}$	-46.8	-47.0	-50.0	-50.0
$\text{MnN}(\text{CN})_4^{2-} + \text{H}_2\text{O} + \text{CH}_2\text{CH}_2\text{O} + 2\text{CH}_3\text{COOH}$	-44.6	-63.9	-58.6	-78.0

Table S2 Successive runs of catalytic epoxidation of 2-methyl-2-pentene by $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$ ^a

No. of runs	accumulated epoxide yield (%) ^b	
	With $\text{CH}_3\text{CO}_2\text{H}$	No $\text{CH}_3\text{CO}_2\text{H}$ ^c
1	96	90
2	94	90
3	86	92
4	78	93
5	71	94
7	-	95
10	-	96
13	-	96

^a Reaction conditions for the 1st run: $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ (1 mol%), CH_3CN (1 mL), $\text{CH}_3\text{CO}_2\text{H}$ (1 mmol), 2-methyl-2-pentene (1 mmol), argon atmosphere, $T = 23$ °C, 30 min; reaction conditions for the other runs: 2-methyl-2-pentene (1 mmol), $\text{CH}_3\text{CO}_2\text{H}$ (1 mmol) and H_2O_2 in H_2O (1 mmol), $T = 23$ °C, 30 min. ^b % yield based on the total amount of 2-methyl-2-pentene added. ^c No $\text{CH}_3\text{CO}_2\text{H}$ was added in all runs.

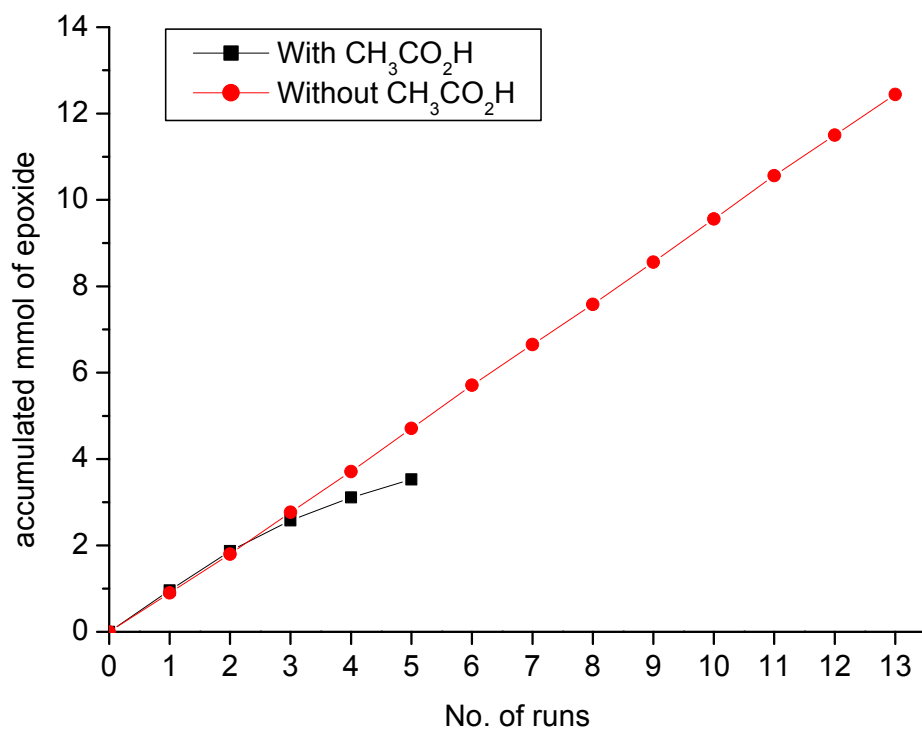


Figure S1 Plot of accumulated mmol of epoxide vs. number of consecutive runs of epoxidation of 2-methyl-2-pentene by $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$

Table S3 Effects of catalyst loadings on the catalytic epoxidation of 2-methyl-2-pentene by $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2^a$

Entry	catalyst loading (%)	H_2O_2 (equiv.)	Conv. (%)	Epoxide yield (%) ^b	Time
1	1.0 ^c	1.05	100	96	5 min
2	0.1 ^d	1.05	100	95	15 min
3	0.05 ^d	1.05	94	90 (turnover 1800)	1.5 h
4	1.0	1	100	90	10 min
5	0.1	1	98	89	6 h
6	0.05	1	91	88	1 d

^a Reaction conditions: 2-methyl-2-pentene (1 mmol), CH_3CN (1 mL), argon atmosphere, $T = 23\text{ }^\circ\text{C}$. ^b % yield based on the amount of substrate. ^c 0.1 mmol $\text{CH}_3\text{CO}_2\text{H}$ was added. ^d 1 mmol $\text{CH}_3\text{CO}_2\text{H}$ was added.

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