

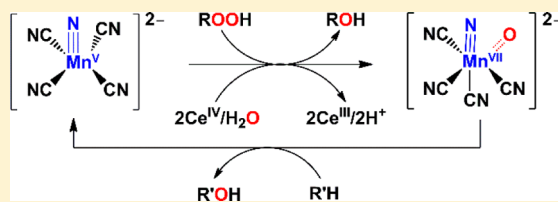
# Highly Efficient Alkane Oxidation Catalyzed by $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$ . Evidence for $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$ as an Active Intermediate

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**S** Supporting Information

**ABSTRACT:** The oxidation of various alkanes catalyzed by  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$  using various terminal oxidants at room temperature has been investigated. Excellent yields of alcohols and ketones (>95%) are obtained using  $\text{H}_2\text{O}_2$  as oxidant and  $\text{CF}_3\text{CH}_2\text{OH}$  as solvent. Good yields (>80%) are also obtained using  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$  in  $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ . Kinetic isotope effects (KIEs) are determined by using an equimolar mixture of cyclohexane ( $c\text{-C}_6\text{H}_{12}$ ) and cyclohexane- $d_{12}$  ( $c\text{-C}_6\text{D}_{12}$ ) as substrate. The KIEs are  $3.1 \pm 0.3$  and  $3.6 \pm 0.2$  for oxidation by  $\text{H}_2\text{O}_2$  and  $\text{Ce}(\text{IV})$ , respectively. On the other hand, the rate constants for the formation of products using  $c\text{-C}_6\text{H}_{12}$  or  $c\text{-C}_6\text{D}_{12}$  as single substrate are the same. These results are consistent with initial rate-limiting formation of an active intermediate between  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$  and  $\text{H}_2\text{O}_2$  or  $\text{Ce}^{\text{IV}}$ , followed by H-atom abstraction from cyclohexane by the active intermediate. When  $\text{PhCH}_2\text{C}(\text{CH}_3)_2\text{OOH}$  (MPPH) is used as oxidant for the oxidation of  $c\text{-C}_6\text{H}_{12}$ , the major products are  $c\text{-C}_6\text{H}_{11}\text{OH}$ ,  $c\text{-C}_6\text{H}_{10}\text{O}$ , and  $\text{PhCH}_2\text{C}(\text{CH}_3)_2\text{OH}$  (MPPOH), suggesting heterolytic cleavage of MPPH to generate a  $\text{Mn}=\text{O}$  intermediate. In the reaction of  $\text{H}_2\text{O}_2$  with  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$  in  $\text{CF}_3\text{CH}_2\text{OH}$ , a peak at  $m/z$  628.1 was observed in the electrospray ionization mass spectrometry, which is assigned to the solvated manganese nitrido oxo species,  $(\text{PPh}_4)[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-} \cdot \text{CF}_3\text{CH}_2\text{OH}$ . On the basis of the experimental results the proposed mechanism for catalytic alkane oxidation by  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}/\text{ROOH}$  involves initial rate-limiting O-atom transfer from ROOH to  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$  to generate a manganese(VII) nitrido oxo active species,  $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$ , which then oxidizes alkanes ( $\text{R}'\text{H}$ ) via a H-atom abstraction/O-rebound mechanism. The proposed mechanism is also supported by density functional theory calculations.



## INTRODUCTION

The search for efficient catalysts for selective oxidation of alkanes under mild conditions continues to be a challenge for chemists.<sup>1</sup> We have been interested in the design of highly active alkane oxidation systems that consist of an earth abundant metal catalyst such as Mn or Fe, and a green oxidant such as  $\text{O}_2$  or  $\text{H}_2\text{O}_2$ . Although a number of  $\text{Mn}(\text{II})/(\text{III})/(\text{IV})$  alkane oxidation catalysts are known,<sup>2–6</sup> the product yields are generally low (<50%) using green oxidants such as  $\text{H}_2\text{O}_2$ .

We recently reported that the square pyramidal  $\text{Mn}(\text{V})$  nitrido complex  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ , prepared by Wieghardt and co-workers,<sup>7</sup> is a very active and selective catalyst for the oxidation of alkenes and alcohols in  $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$  using  $\text{H}_2\text{O}_2$  as the oxidant, with product yields close to 100%.<sup>8</sup> Although in a high oxidation state, the  $d^2$   $\text{Mn}(\text{V})$  complex is relatively stable compared with many high-spin  $\text{Mn}(\text{II})/(\text{III})$  catalysts. Binding of oxidant to  $\text{Mn}(\text{V})$  is facilitated by the presence of a vacant site. According to density functional theory (DFT) calculations,  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  first binds to  $\text{H}_2\text{O}_2$  to form the intermediate  $[\text{Mn}(\text{N})(\text{CN})_4(\text{H}_2\text{O}_2)]^{2-}$ ; the coordinated  $\text{H}_2\text{O}_2$  is stabilized by hydrogen bonding with the  $\text{CN}^-$  ligands and  $\text{CH}_3\text{COOH}$ .<sup>8</sup>

We report here that when  $\text{CF}_3\text{CH}_2\text{OH}$  is used as the solvent,  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  is also a highly efficient catalyst for the

oxidation of alkanes using  $\text{H}_2\text{O}_2$  and various other oxidants, with unprecedented yields of >95%. Through a combination of experimental and computational studies, we provide evidence that the active intermediate is a manganese(VII) nitrido oxo species,  $[\text{Mn}(\text{N})(\text{O})(\text{CN})_4]^{2-}$ . Our work suggests that  $d^2$   $\text{Mn}(\text{V})$  nitrido complexes are potentially a new class of highly efficient oxidation catalysts that may be more active and more robust than conventional  $\text{Mn}(\text{II})/(\text{III})/(\text{IV})$  oxidation catalysts.

## EXPERIMENTAL SECTION

**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.<sup>7</sup> The purity of the complex was determined by CHN elemental analysis and UV/vis spectrophotometry. All organic substrates were obtained from Sigma-Aldrich and purified according to literature methods.<sup>9</sup> Hydrogen peroxide (33%, Sigma-Aldrich) was used as received and standardized by iodometry.<sup>10,11</sup> 2-Methyl-1-phenyl-2-propyl hydroperoxide (MPPH) was prepared according to a literature method,<sup>12</sup> and its purity was determined to be >99% by NMR spectroscopy. Active MPPH levels were further measured by iodometric titrations, which showed >99% peroxide activity. Cyclohexane- $d_{12}$  (98+ atom % D) and  $\text{H}_2^{18}\text{O}$  (96 atom %  $^{18}\text{O}$ ) were purchased from Medical

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Table 1. Catalytic Oxidation of Various Alkanes by  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2^a$ 

entry	substrate	product (% yield) <sup>b</sup>	total % yield
1 <sup>c</sup>	cyclohexane	cyclohexanol (11), cyclohexanone (14)	25
2	cyclohexane	cyclohexanol (69), cyclohexanone (28)	97
3 <sup>d</sup>	cyclohexane	cyclohexanol (70), cyclohexanone (26), cyclohexyl bromide (1)	97
4 <sup>e</sup>	cyclohexane	cyclohexanol (8), cyclohexanone (56)	64
5	cycloheptane	cycloheptanol (62), cycloheptanone (35)	97
6	cyclooctane	cyclooctanol (63), cyclooctanone (34)	97
7	<i>n</i> -heptane	2-heptanol (22), 3-heptanol (25), 4-heptanol (13), 2-heptanone (15), 3-heptanone (17), 4-heptanone (4)	96
8	<i>n</i> -octane	2-octanol (17), 3-octanol (19), 4-octanol (18), 2-octanone (15), 3-octanone (14), 4-octanone (14)	97
9	2,3-dimethylbutane	2,3-dimethyl-2-butanol (96)	96
10	<i>trans</i> -1,2-dimethylcyclohexane	<i>trans</i> -1,2-dimethylcyclohexanol (36), <i>cis</i> -1,2-dimethylcyclohexanol (1), 2,3-dimethylcyclohexanol (19), 3,4-dimethylcyclohexanol (14), 2,3- and 3,4-dimethylcyclohexanone (25)	95
11	<i>cis</i> -1,2-dimethylcyclohexane	<i>cis</i> -1,2-dimethylcyclohexanol (84), <i>trans</i> -1,2-dimethylcyclohexanol (1), 2,3-dimethylcyclohexanol (4), 3,4-dimethylcyclohexanol (5), 2,3- and 3,4-dimethylcyclohexanone (2)	96

<sup>a</sup>Reaction conditions:  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ , 2.5 mM; alkane, 1.2 M;  $\text{H}_2\text{O}_2$ , 0.25 M;  $\text{CH}_3\text{CO}_2\text{H}$ , 0.25 M; solvent,  $\text{CF}_3\text{CH}_2\text{OH}$ ;  $T = 23^\circ\text{C}$ , under argon. Time, 5 h. <sup>b</sup>% yield of alcohol = (mol of alcohol/mol of  $\text{H}_2\text{O}_2$ )  $\times$  100; % yield of ketone = (mol of ketone/mol of  $\text{H}_2\text{O}_2$ )  $\times$  2  $\times$  100. <sup>c</sup> $\text{CH}_3\text{CN}$  was used as solvent. <sup>d</sup>In the presence of 0.5 M  $\text{BrCCl}_3$ . <sup>e</sup>Reaction conditions:  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ , 0.5 mM; cyclohexane, 4.0 M;  $\text{H}_2\text{O}_2$ , 0.75 M;  $\text{CH}_3\text{CO}_2\text{H}$ , 0.5 M; solvent,  $\text{CF}_3\text{CH}_2\text{OH}$ .  $T = 23^\circ\text{C}$ . Time, 48 h. TON = 960.

Isotopes and used as received.  $\text{H}_2^{18}\text{O}$  (90 atom %  $^{18}\text{O}$ ) was obtained from Icon Services Inc. Bromotrichloromethane was purchased from Aldrich and was purified by passing through a short column of neutral alumina prior to use.

**Instrumentation.** Gas chromatographic (GC) analyses were performed on a HP5890 GC/FID gas chromatograph equipped with a DB-FFAP (30 m  $\times$  0.25 mm i.d.) or a HP-5MS (30 m  $\times$  0.25 mm i.d.) capillary column. GC/MS measurements were carried out on a HP6890 gas chromatograph interfaced to a HP5975 mass selective detector. Elemental analyses were done on an Elementar Vario EL analyzer. Mn content was determined by a PerkinElmer Optima 2100 DV ICP optical emission spectrometer. Electrospray ionization mass spectrometry (ESI/MS) was performed on an Applied Biosystems 3200 Q-trap mass spectrometer.

**Catalytic Oxidation of Alkanes.** Typically the oxidant was added to a pink solution of  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$  in  $\text{CF}_3\text{CH}_2\text{OH}$  containing substrate and acetic acid at  $23^\circ\text{C}$ . The mixture was vigorously stirred under argon. Chlorobenzene was then added as an internal standard, and the mixture was analyzed by GC and GC/MS at various time intervals. <sup>t</sup>BuOOH and MPPH were added using a syringe pump at 10–25  $\mu\text{L}/\text{min}$ .

For catalytic oxidation with MPPH, product analysis was carried out when all MPPH was consumed, since MPPH itself will decompose in the GC injection port to give a variety of products. The consumption of MPPH was monitored by adding  $\text{PPh}_3$  to the solution; when an aliquot of the solution did not produce any  $\text{PPh}_3=\text{O}$  (as monitored by GC) from  $\text{PPh}_3$ , then it was assumed that all MPPH was consumed.

Kinetic isotope effects (KIEs) were investigated by using an equimolar mixture of cyclohexane and cyclohexane-*d*<sub>12</sub> 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.

For  $^{18}\text{O}$ -labeling experiments, the  $^{16}\text{O}/^{18}\text{O}$  compositions of cyclohexanol and cyclohexanone were determined from the relative abundances of the peaks at  $m/z = 100(^{16}\text{O})$ ,  $102(^{18}\text{O})$  for cyclohexanol and  $98(^{16}\text{O})$ ,  $100(^{18}\text{O})$  for cyclohexanone in GC/MS(EI).

**Isolation of Solid from Oxidation of Mn(V).**  $\text{H}_2\text{O}_2$  (12.5 mmol) was added to a pink solution of  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$  (0.125 mmol) in 15 mL of  $\text{CF}_3\text{CH}_2\text{OH}$  containing 1 mL of cyclohexane and 12.5 mmol of acetic acid at  $23^\circ\text{C}$ . The mixture was stirred under argon for 6 h. The resulting pale pink precipitate was collected by filtration, washed with water, acetone, dichloromethane, and dried in vacuo. Yield: 15 mg (56%). IR (KBr  $\text{cm}^{-1}$ ):  $\nu(\text{CN})$  2151. Elemental analysis calcd (%) for  $\text{Mn}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ : Mn 25.79; C 22.55; H 2.84; N 26.30; found: Mn 25.80; C 22.85; H 3.21; N 25.92.

**DFT Calculations.** All optimizations and frequency calculations were done at the B3LYP (Becke three-parameter Lee–Yang–Parr

hybrid functional)<sup>13</sup> level using LanL2DZ basis set<sup>14</sup> for Mn and 6-311+G(d,p) basis set for nonmetal atoms. The solvent effect of  $\text{CF}_3\text{CH}_2\text{OH}$  (TFE) was taken into account by the polarizable continuum model.<sup>15</sup> The geometries were fully optimized without any symmetry or geometry constraint. The nature of all stationary points was confirmed by vibrational frequencies calculations. All reactants, intermediates, and products have no imaginary frequency, while all transition states have only one imaginary frequency. The connectivity of transition state structures were confirmed by intrinsic reaction coordinates (IRC) calculations. The natural bond orbital (NBO) analyses<sup>16</sup> were carried out on the  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  complex and INT5 obtained at the B3LYP level.

## RESULTS AND DISCUSSION

**Catalytic Oxidation of Alkanes.** Although  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  is a highly efficient catalyst for the oxidation of alkenes and alcohols in  $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$  by  $\text{H}_2\text{O}_2$  at room temperature, when excess cyclohexane was used as substrate under the same conditions, the product yield was only 25% (Table 1, entry 1). However, when  $\text{CF}_3\text{CH}_2\text{OH}$  was used as the solvent instead of  $\text{CH}_3\text{CN}$ , the yield became 85%, which was further increased to 97% (turnover number, TON = 97) when a small amount of acetic acid (0.25 M) was added (entry 2). By adding more substrate and oxidant, a TON of 960 could be achieved (entry 4). High yields of >95% were also obtained in the oxidation of various other alkanes. For linear alkanes, oxidation occurred only at the secondary C–H bonds (entry 7–8); no products arising from oxidation of primary C–H bonds were observed for these substrates. In the oxidation of *trans*- and *cis*-1,2-dimethylcyclohexane, only 1% of epimerized products were observed (entry 10–11), suggesting that there are no freely diffusing alkyl radicals in the catalytic reaction. This is also supported by the formation of only 1% bromocyclohexane in the oxidation of cyclohexane in the presence of  $\text{BrCCl}_3$ , which is an efficient scavenger for alkyl radicals (entry 3).

The oxidation of secondary C–H bonds produced a mixture of the corresponding alcohols and ketones. The ketone was probably derived from oxidation of the initial alcohol product. In the competitive oxidation of a mixture of cycloheptanol and cyclohexane (in a mole ratio of 1:1) by  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}/\text{H}_2\text{O}_2$ , the products consisted of 34% cycloheptanone, 8% cyclohexanol, and 7% cyclohexanone, indicating that alcohol is more rapidly oxidized than alkane by this system.<sup>17</sup>

Various other oxidants have also been used (Table 2). Good yields (85%) of cyclohexanol and cyclohexanone were also

**Table 2. Effects of Various Oxidants on the Catalytic Oxidation of Cyclohexane by  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]^{a,c}$**

entry	oxidant	time (h)	product (% yield)		
			alcohol	ketone	total yield (%)
1	<sup>t</sup> BuOOH	8	40	45	85
2	oxone	5	13	22	35
3	$\text{CH}_3\text{CO}_3\text{H}$	5	14	6	20
4	<i>m</i> -CPBA	0.5	37	7	44
5 <sup>b</sup>	Ce(IV)	0.5	38	49	87
6	$\text{Cl}_2\text{pyO}$	5	trace	0	0

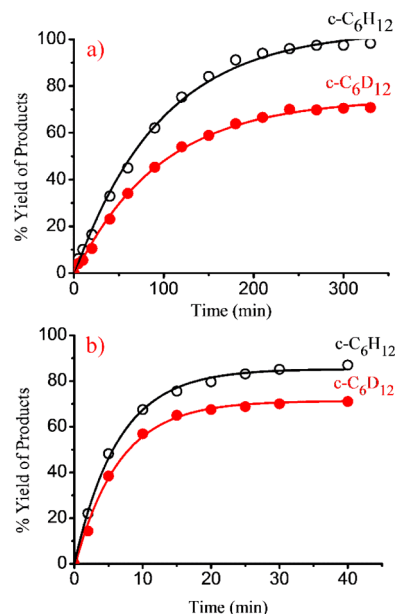
<sup>a</sup>Reaction conditions:  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ , 2.5 mM; cyclohexane, 1.2 M; oxidant, 0.25 M;  $\text{CH}_3\text{CO}_2\text{H}$ , 0.25 M; solvent,  $\text{CF}_3\text{CH}_2\text{OH}$ ;  $T = 23^\circ\text{C}$ , under argon. <sup>b</sup> $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$  (7:3 v/v) was used as solvent. Yield was calculated based on Ce(IV) acting as a one-electron oxidant.

obtained using <sup>t</sup>BuOOH. However, oxone ( $\text{NaHSO}_5$ ), peracetic acid ( $\text{CH}_3\text{CO}_3\text{H}$ ), and *m*-chloroperbenzoic acid (*m*-CPBA) gave much lower yields, while 2,6-dichloropyridine N-oxide ( $\text{Cl}_2\text{pyO}$ ) was completely ineffective. Interestingly, the one-electron oxidant  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]\{\text{Ce}(\text{IV})\}$  gave a high yield of 87% in  $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$  (7:3 v/v) within 30 min. The yield is similar (85%) when the oxidation was carried out in  $\text{CF}_3\text{CH}_2\text{OH}/0.1\text{ M } \text{CF}_3\text{CO}_2\text{H}$  in  $\text{H}_2\text{O}$  (7:3 v/v) (Table 3, entry 2). When the Ce(IV) oxidation was carried out in  $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2^{18}\text{O}$  (96% <sup>18</sup>O-labeled), the cyclohexanol and cyclohexanone produced were 85% and 87% <sup>18</sup>O-labeled, respectively, indicating that the oxygen source came from water. Oxidation of various alkanes using Ce(IV) also gave good yields (Table 3). As in the case of  $\text{H}_2\text{O}_2$ , only oxidation of secondary C–H bonds was observed in the oxidation of linear alkanes. Also, in the oxidation of *trans*- and *cis*-1,2-dimethylcyclohexane, <1% of epimerized products were observed.

**Kinetic Isotope Effects.** KIEs were determined by using an equimolar mixture of cyclohexane (*c*- $\text{C}_6\text{H}_{12}$ ) and cyclohexane-*d*<sub>12</sub> (*c*- $\text{C}_6\text{D}_{12}$ ) as a substrate. The KIEs for oxidation by  $\text{H}_2\text{O}_2$  and Ce(IV) were found to be  $3.1 \pm 0.3$  and  $3.6 \pm 0.2$ , respectively (Table S2, Supporting Information).

Kinetic studies for catalytic cyclohexane oxidation by  $\text{H}_2\text{O}_2$  and Ce(IV) were also performed using *c*- $\text{C}_6\text{H}_{12}$  or *c*- $\text{C}_6\text{D}_{12}$  as a single substrate. For both oxidants, the formation of products (determined by GC) followed pseudo-first-order kinetics. In

oxidation by  $\text{H}_2\text{O}_2$  the pseudo-first-order rate constants ( $k_{\text{obs}}$ ) for *c*- $\text{C}_6\text{H}_{12}$  and *c*- $\text{C}_6\text{D}_{12}$  are  $(1.05 \pm 0.05) \times 10^{-2}$  and  $(1.06 \pm 0.07) \times 10^{-2} \text{ min}^{-1}$ , respectively, at  $[\text{cyclohexane}] = 1.2 \text{ M}$  and  $23^\circ\text{C}$  (Figure 1a). The same rate constants observed for the oxidation



**Figure 1.** Pseudo-first-order fit of % yield vs time for the catalytic oxidation of *c*- $\text{C}_6\text{H}_{12}$  (1.2 M) and *c*- $\text{C}_6\text{D}_{12}$  (1.2 M) by  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$  (2.5 mM) in the presence of  $\text{CH}_3\text{CO}_2\text{H}$  (0.25 M) at  $23^\circ\text{C}$ . (a) Oxidant =  $\text{H}_2\text{O}_2$  (0.25 M) in  $\text{CF}_3\text{CH}_2\text{OH}$ . (b) Oxidant = Ce(IV) (0.25 M) in  $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$  (7:3 v/v).

of *c*- $\text{C}_6\text{H}_{12}$  and *c*- $\text{C}_6\text{D}_{12}$ , despite a KIE of 3.1 obtained from competition experiments, suggest that the rate-limiting step in the catalytic reaction is the formation of the active intermediate between  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  and  $\text{H}_2\text{O}_2$ , followed by H-atom abstraction from cyclohexane by the active intermediate (see Discussion). When 0.5 M of cyclohexane was used, the yields became lower, but the rate constants remained the same:  $(1.04 \pm 0.07) \times 10^{-2} \text{ min}^{-1}$  and  $(1.06 \pm 0.05) \times 10^{-2} \text{ min}^{-1}$  for *c*- $\text{C}_6\text{H}_{12}$  and *c*- $\text{C}_6\text{D}_{12}$ , respectively (Table S3 and Figure S1a, Supporting Information). Similarly, in oxidation by Ce(IV),  $k_{\text{obs}}$  values for *c*- $\text{C}_6\text{H}_{12}$  and *c*- $\text{C}_6\text{D}_{12}$  are the same:  $(1.56 \pm 0.07) \times 10^{-1}$  and  $(1.55 \pm 0.05) \times 10^{-1} \text{ min}^{-1}$ , respectively at  $[\text{cyclohexane}] = 1.2 \text{ M}$  and  $23^\circ\text{C}$  (Figure 1b), suggesting that the formation of the active

**Table 3. Catalytic Oxidation of Various Alkanes by  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]/\text{Ce}(\text{IV})^{a,c}$**

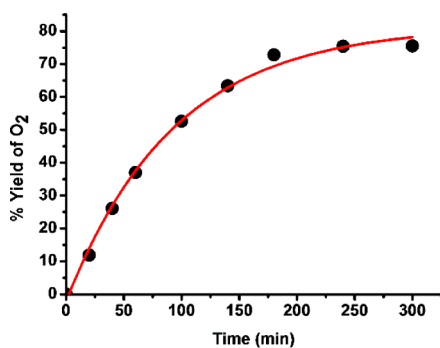
entry	substrate	product (% yield) <sup>b</sup>	total % yield
1	cyclohexane	cyclohexanol (38), cyclohexanone (49)	87
2 <sup>c</sup>	cyclohexane	cyclohexanol (41%), cyclohexanone (44%)	85
3	cycloheptane	cycloheptanol (39), cycloheptanone (41)	80
4	cyclooctane	cyclooctanol (31), cyclooctanone (41)	72
5	<i>n</i> -heptane	2-heptanol (18), 3-heptanol (19), 4-heptanol (10), 2-heptanone (7), 3-heptanone (8), 4-heptanone (5)	67
6	2,3-dimethylbutane	2,3-dimethyl-2-butanol (90)	90
7	<i>trans</i> -1,2-dimethylcyclohexane	<i>trans</i> -1,2-dimethylcyclohexanol (8), <i>cis</i> -1,2-dimethylcyclohexanol (trace), 2,3-dimethylcyclohexanol (29), 3,4-dimethylcyclohexanol (7), 2,3- and 3,4-dimethylcyclohexanone (36)	80
8	<i>cis</i> -1,2-dimethylcyclohexane	<i>cis</i> -1,2-dimethylcyclohexanol (75), <i>trans</i> -1,2-dimethylcyclohexanol (1), 2,3-dimethylcyclohexanol (8), 3,4-dimethylcyclohexanol (2), 2,3- and 3,4-dimethylcyclohexanone (3)	89

<sup>a</sup>Reaction condition:  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ , 2.5 mM; alkane, 1.2 M;  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ , 0.25 M;  $\text{CH}_3\text{CO}_2\text{H}$ , 0.25 M; solvent,  $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$  (7:3 v/v);  $T = 23^\circ\text{C}$ . Time = 0.5 h. <sup>b</sup>% yield of alcohol = (mmol of alcohol/mmol of  $\text{Ce}(\text{IV})$ )  $\times 2 \times 100\%$ . % yield of ketone = (mmol of ketone/mmol of  $\text{Ce}(\text{IV})$ )  $\times 4 \times 100\%$ . <sup>c</sup>Reaction carried out in  $\text{CF}_3\text{CH}_2\text{OH}/0.1\text{ M } \text{CF}_3\text{CO}_2\text{H}$  in  $\text{H}_2\text{O}$  (7:3 v/v).

intermediate between  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  and  $\text{Ce}(\text{IV})$  is also rate-limiting. Again the yields are lower but the rate constants are unchanged when [cyclohexane] was decreased to 0.5 M:  $(1.57 \pm 0.10) \times 10^{-1}$  and  $(1.55 \pm 0.08) \times 10^{-1} \text{ min}^{-1}$  for  $c\text{-C}_6\text{H}_{12}$  and  $c\text{-C}_6\text{D}_{12}$ , respectively. The oxidation of  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  by  $\text{Ce}(\text{IV})$ , however, is about 15 times faster than oxidation by  $\text{H}_2\text{O}_2$ .

The kinetics have also been studied at various temperatures. Activation parameters obtained from Eyring plots (Figure S2, Supporting Information) are  $\Delta H^\ddagger = 16.2 \pm 1.5 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -(20 \pm 4) \text{ cal mol}^{-1} \text{ K}^{-1}$  for  $\text{H}_2\text{O}_2$ ;  $\Delta H^\ddagger = 17.1 \pm 1.0 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -(13 \pm 3) \text{ cal mol}^{-1} \text{ K}^{-1}$  for  $\text{Ce}(\text{IV})$ . The negative  $\Delta S$  values are consistent with the proposed bimolecular reaction between  $\text{Mn}(\text{V})$  and the oxidant in the rate-limiting step.

**Reaction of Mn(V) with Oxidant in the Absence of Alkane.** Upon adding  $\text{Ce}(\text{IV})$  or  $\text{H}_2\text{O}_2$  to  $\text{Mn}(\text{V})$  in  $\text{CF}_3\text{CH}_2\text{OH}$ , a pink solid which is insoluble in common solvents was gradually formed. IR shows a  $\nu_{\text{CN}}$  band at  $2151 \text{ cm}^{-1}$ , which is shifted from  $2116 \text{ cm}^{-1}$  in the  $\text{Mn}(\text{V})$  catalyst (Figure S3, Supporting Information). Mn, C, H, and N analyses approximately correspond to the formula “ $\text{Mn}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ ”. This insoluble solid is probably a cyano-bridged Mn-CN-Mn polymer. When the oxidant is  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$  could be detected (by GC/TCD) in 78% yield in the absence of alkane, suggesting that  $\text{Mn}(\text{V})$  also catalyzes the disproportionation of  $\text{H}_2\text{O}_2$ . The kinetics of this reaction has been followed by monitoring the yield of  $\text{O}_2$  as a function of time (Figure 2).  $k_{\text{obs}}$  was found to be  $(1.08 \pm 0.09) \times$

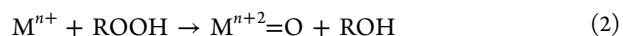
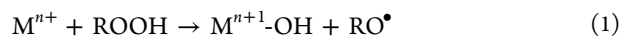


**Figure 2.** Pseudo-first-order fit of % yield of  $\text{O}_2$  vs time for the reaction of  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$  (2.5 mM) and  $\text{H}_2\text{O}_2$  (0.25 M) in 1 mL of  $\text{CF}_3\text{CH}_2\text{OH}$  at  $23^\circ\text{C}$ . % Yield =  $(\text{mmol of O}_2 / 1/2 \text{ mmol of H}_2\text{O}_2) \times 100\%$ .

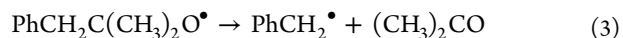
$10^{-2} \text{ min}^{-1}$  at  $23^\circ\text{C}$ , which is the same as the rate constant for cyclohexane oxidation by  $\text{Mn}(\text{V})/\text{H}_2\text{O}_2$ , again in accordance with the formation of the active species between  $\text{Mn}(\text{V})$  and  $\text{H}_2\text{O}_2$  being the rate-limiting step. In the presence of excess  $\text{C}_6\text{H}_{12}$  (1.2 M), <1%  $\text{O}_2$  could be detected, indicating that oxidation of  $\text{C}_6\text{H}_{12}$  by the active species competes effectively with the disproportionation of  $\text{H}_2\text{O}_2$ . However, when excess  $\text{C}_6\text{D}_{12}$  (1.2 M) was used as substrate, 22%  $\text{O}_2$  could be detected; in this case the competing  $\text{H}_2\text{O}_2$  disproportionation reaction becomes significant, as a result of the slower rate of oxidation of  $\text{C}_6\text{D}_{12}$  by the active species. This is the main reason for the lower yield of organic products for  $\text{C}_6\text{D}_{12}$  (71%) than for  $\text{C}_6\text{H}_{12}$  (97%, Figure 1a and Table S3, Supporting Information). We were unable to obtain higher TON due to the gradual decomposition of the catalyst to an insoluble solid. Formation of this solid also caused the solution to become turbid, and hence we were unable to

study the kinetics of the catalytic oxidation by UV/vis spectrophotometry (Figure S4, Supporting Information).

**Catalytic Oxidation with  $\text{PhCH}_2\text{C}(\text{CH}_3)_2\text{OOH}$  (MPPH).** The interaction of a metal catalyst with a peroxide ( $\text{ROOH}$ ) may occur by homolytic (eq 1) or heterolytic (eq 2) pathways to generate intermediates that can abstract H-atoms from alkanes.



In order to distinguish between these possibilities when  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  is used as catalyst, we carried out catalytic cyclohexane oxidation using  $\text{PhCH}_2\text{C}(\text{CH}_3)_2\text{OOH}$  (MPPH) as the oxidant. MPPH has been used as a mechanistic probe to distinguish between free radical ( $\text{RO}^\bullet$  from homolytic cleavage) and metal-based ( $\text{M}=\text{O}$  from heterolytic cleavage) hydrocarbon oxidation.<sup>12,18</sup> When MPPH undergoes homolytic O–O bond cleavage, the resulting *tert*-alkoxyl radical ( $\text{PhCH}_2\text{C}(\text{CH}_3)_2\text{O}^\bullet$ ) is known to undergo very rapid  $\beta$ -scission (eq 3); thus H-atom abstraction from an alkane by  $\text{PhCH}_2\text{C}(\text{CH}_3)_2\text{O}^\bullet$  cannot occur. Subsequent reactions of  $\text{PhCH}_2^\bullet$  will result in products such as  $\text{PhCH}_2\text{OH}$  and  $\text{PhCHO}$ . On the other hand, heterolytic cleavage of MPPH will result in the formation of  $\text{PhCH}_2\text{C}(\text{CH}_3)_2\text{OH}$  (MPPOH) and  $\text{M}=\text{O}$  (eq 2); the latter species can oxidize RH to give ROH.



When MPPH was used as oxidant, apparently products arising from both heterolytic (MPPOH, cyclohexanol, and cyclohexanone) and homolytic cleavage (benzyl alcohol and benzaldehyde) of MPPH were observed (Table 4). However,

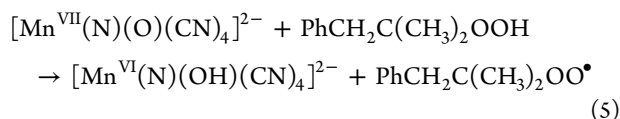
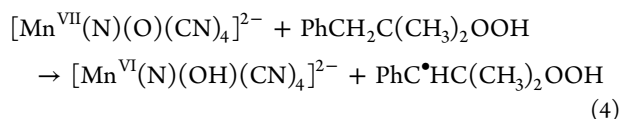
**Table 4.** Catalytic Oxidation of Cyclohexane by  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]/\text{MPPH}^a$

substrate	products (% yield)	
	heterolytic cleavage	homolytic cleavage
$c\text{-C}_6\text{H}_{12}^b$	$c\text{-C}_6\text{H}_{11}\text{OH}$ (9), $c\text{-C}_6\text{H}_{10}\text{O}$ (3), MPPOH (65)	$\text{PhCH}_2\text{OH}$ (16), $\text{PhCHO}$ (14), $(\text{CH}_3)_2\text{CO}$ (27)
$c\text{-C}_6\text{H}_{12}^c$	$c\text{-C}_6\text{H}_{11}\text{OH}$ (12), $c\text{-C}_6\text{H}_{10}\text{O}$ (48), MPPOH (75)	$\text{PhCH}_2\text{OH}$ (11), $\text{PhCHO}$ (7), $(\text{CH}_3)_2\text{CO}$ (16)
$c\text{-C}_8\text{H}_{16}^b$	$c\text{-C}_8\text{H}_{15}\text{OH}$ (25), $c\text{-C}_8\text{H}_{14}\text{O}$ (36), MPPOH (78)	$\text{PhCH}_2\text{OH}$ (9), $\text{PhCHO}$ (11), $(\text{CH}_3)_2\text{CO}$ (20)
$c\text{-C}_8\text{H}_{16}^c$	$c\text{-C}_8\text{H}_{15}\text{OH}$ (18), $c\text{-C}_8\text{H}_{14}\text{O}$ (62), MPPOH (90)	$\text{PhCH}_2\text{OH}$ (4), $\text{PhCHO}$ (5), $(\text{CH}_3)_2\text{CO}$ (8)
Nil <sup>c</sup>	MPPOH (54)	$\text{PhCH}_2\text{OH}$ (15), $\text{PhCHO}$ (30), $(\text{CH}_3)_2\text{CO}$ (44)

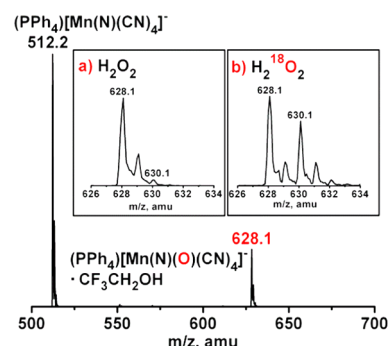
<sup>a</sup>Reaction conditions: substrate, 1.2 M; solvent,  $\text{CF}_3\text{CH}_2\text{OH}$ ,  $T = 23^\circ\text{C}$ . <sup>b</sup> $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ , 2.5 mM; MPPH, 25 mM. <sup>c</sup> $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ , 1 mM; MPPH, 10 mM. Theoretically yield of MPPOH +  $(\text{CH}_3)_2\text{CO}$  (=  $\text{PhCH}_2\text{OH}$  +  $\text{PhCHO}$ ) = 100%.

it is possible that apart from reacting with cyclohexane, the  $\text{Mn}=\text{O}$  species generated from heterolytic cleavage of MPPH may also abstract an H-atom from the relatively weak benzylic C–H or O–H bonds of MPPH (eqs 4 and 5). The resulting radicals would decompose to benzyl alcohol, benzaldehyde, and other organic products. The overall reaction is disproportionation of MPPH catalyzed by  $\text{Mn}(\text{V})$ , which is not unexpected since we have demonstrated in the above section that  $\text{Mn}(\text{V})$  also catalyzes disproportionation of  $\text{H}_2\text{O}_2$ . To confirm this disproportionation,  $\text{Mn}(\text{V})$  was treated with excess MPPH in

the absence of alkane. It was found that the MPPH was readily decomposed, and the yield of MPPOH is approximately equal to that of acetone (which should be equal to yield of benzyl alcohol + benzaldehyde), consistent with catalytic disproportionation of MPPH (Table 4, entry 5). This disproportionation reaction may account for the low yields of cyclohexanol and cyclohexanone (Table 4, entry 1,  $[\text{Mn}]/[\text{MPPH}]/[\text{c-C}_6\text{H}_{12}] = 1:10:48$ ). On the other hand, when lower concentrations of catalyst and MPPH were used, the yields of MPPOH, cyclohexanol, and cyclohexanone increased (Table 4, entry 2,  $[\text{Mn}]/[\text{MPPH}]/[\text{c-C}_6\text{H}_{12}] = 1:10:120$ ), in accordance with a faster rate of reaction of  $\text{Mn}=\text{O}$  with cyclohexane than with MPPH. Moreover, when cyclooctane, which has a lower C–H bond dissociation energy ( $92.6 \text{ kcal mol}^{-1}$ ) than cyclohexane ( $95.4 \text{ kcal mol}^{-1}$ ) was used, the yields of products arising from heterolytic cleavage of MPPH are much higher than those arising from homolytic cleavage (Table 4, entry 3–4). On the basis of these results, we conclude that catalytic alkane oxidation by MPPH occurs predominantly via a heterolytic cleavage mechanism to generate  $\text{Mn}^{\text{VII}}=\text{O}$  and MPPOH. When  $^t\text{BuOOH}$  was used as oxidant, no mixed peroxides such as  $\text{c-C}_6\text{H}_{11}\text{OOCMe}_3$  could be detected, suggesting that homolytic cleavage of  $^t\text{BuOOH}$  to generate  $^t\text{BuO}\cdot$  also does not occur.<sup>12,18</sup>



**Detection of Active Intermediate by ESI/MS.** We then attempted to detect the active intermediate in catalytic alkane oxidation by electrospray ionization mass spectrometry (ESI/MS). The mass spectrum of  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$  in  $\text{CF}_3\text{CH}_2\text{OH}$  exhibits a peak at  $m/z$  512.2, which is assigned to the ion  $\{(\text{PPh}_4)[\text{Mn}(\text{N})(\text{CN})_4]\}^-$  (Figure S5, Supporting Information). At lower  $m/z$ ,  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}\cdot\text{CF}_3\text{CH}_2\text{OH}$  and  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}\cdot 2\text{CF}_3\text{CH}_2\text{OH}$  can also be identified at  $m/z$  136.8 and 186.9, respectively. Intense solvent peaks such as  $[(\text{CF}_3\text{CH}_2\text{OH})(\text{CF}_3\text{CH}_2\text{O})]^-$  and  $[(\text{CF}_3\text{CH}_2\text{OH})_2(\text{CF}_3\text{CH}_2\text{O})]^-$  are also found at  $m/z$  199.3 and 299.3, respectively. When 1.2 equiv of  $\text{H}_2\text{O}_2$  was added to  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ , a new peak at  $m/z$  628.1 was found, which is assigned to the solvated nitrido oxo species,  $(\text{PPh}_4)[\text{Mn}(\text{N})(\text{O})(\text{CN})_4]^- \cdot \text{CF}_3\text{CH}_2\text{OH}$  (Figure 3). MS/MS of this ion ( $m/z$  628.1) shows two peaks at  $m/z$  512.1 and 147.0, which are assigned to  $\{(\text{PPh}_4)[\text{Mn}(\text{N})(\text{CN})_4]\}^-$  and  $[\text{Mn}(\text{N})(\text{CN})_3]^-$ , respectively (Figure S6, Supporting Information). Metal oxo species are known to readily undergo loss of O atoms by collision-induced dissociation in the MS.<sup>19</sup> When  $\text{H}_2^{18}\text{O}_2$  (90%  $^{18}\text{O}$ -labeled) was used, a new peak at  $m/z$  630 appeared, consistent with the species  $\{(\text{PPh}_4)[\text{Mn}(\text{N})(^{18}\text{O})(\text{CN})_4]\}^- \cdot \text{CF}_3\text{CH}_2\text{OH}$  (Figure 3, inset b). Analysis of the relative intensities of the peaks at  $m/z$  628–630 indicates that the manganese oxo species is 45%  $^{18}\text{O}$ -labeled, which could be due to some oxygen exchange between the manganese oxo species and  $\text{H}_2\text{O}$ . This is supported by independent ESI/MS experiments (Figure S7, Supporting Information) on the reaction of  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$  with  $\text{H}_2^{16}\text{O}_2$  in  $\text{CF}_3\text{CH}_2\text{OH}$  containing  $\text{H}_2^{18}\text{O}$  (96%  $^{18}\text{O}$ -labeled), where  $(\text{PPh}_4)[\text{Mn}(\text{N})(^{18}\text{O})(\text{CN})_4]^- \cdot \text{CF}_3\text{CH}_2\text{OH}$  was also

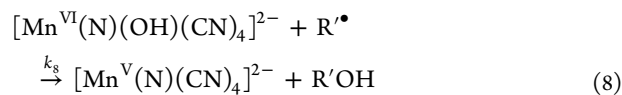
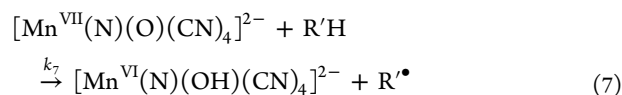
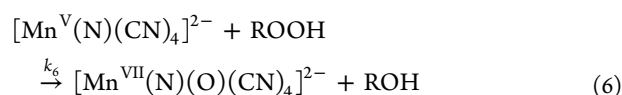


**Figure 3.** Mass spectrum of the reaction mixture of  $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$  (4.5 mM) and  $\text{H}_2\text{O}_2$  (5.3 mM) in  $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$  (9:1 v/v) at 2 min. Insets show the expanded spectra of the peak at  $m/z$  628 when (a)  $\text{H}_2\text{O}_2$  was used; (b)  $\text{H}_2^{18}\text{O}_2$  (90%  $^{18}\text{O}$ -labeled) was used.

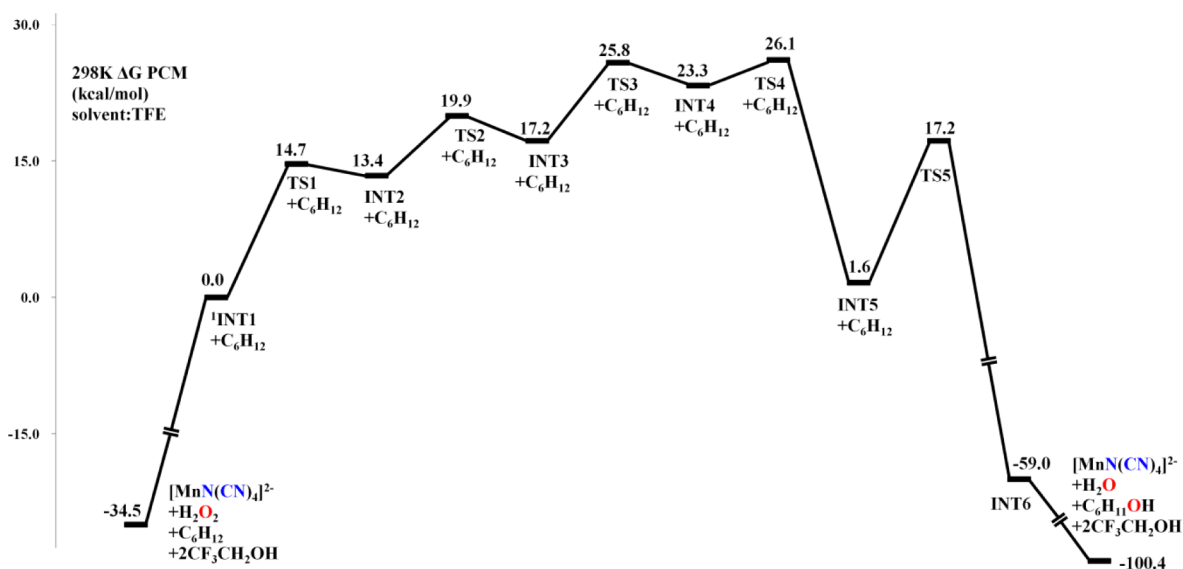
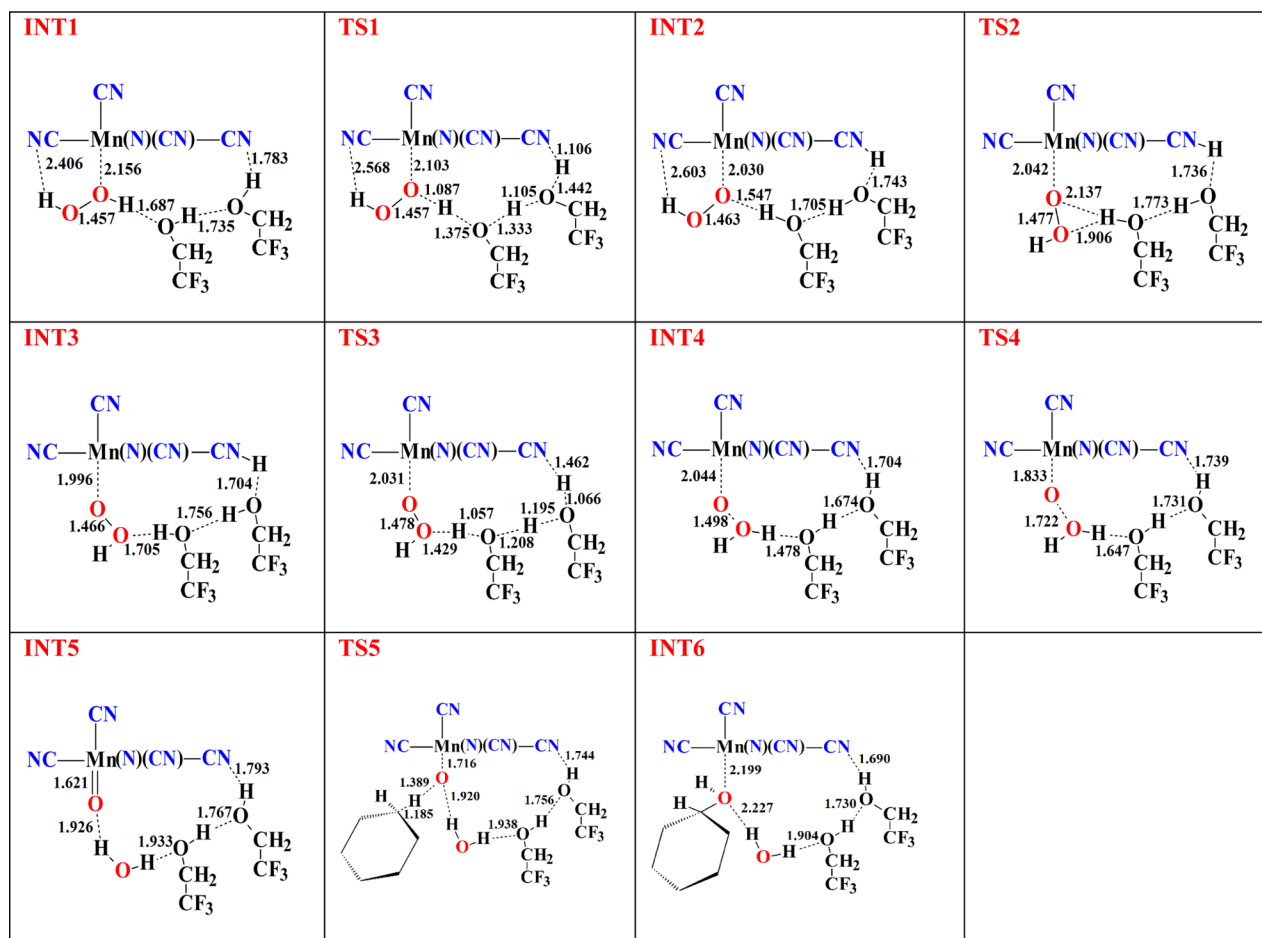
observed at  $m/z = 630$ , and the relatively intensity of this peak increased with time.

On the basis of the ESI/MS data, the rate constant for oxygen exchange between  $\text{Mn}^{\text{VII}}=\text{O}$  and  $\text{H}_2\text{O}$  is estimated to be  $(9 \pm 1) \times 10^{-3} \text{ s}^{-1}$  at  $23^\circ\text{C}$  (Figures S7 and S8, Supporting Information). When  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  was treated with higher concentrations of  $\text{H}_2\text{O}_2$ , a minor peak at  $m/z$  644.1 was also observed, which is tentatively assigned to the nitrido peroxy species,  $(\text{PPh}_4)[\text{Mn}(\text{N})(\text{O}_2)(\text{CN})_4]^- \cdot \text{CF}_3\text{CH}_2\text{OH}$  (Figure S9, Supporting Information).

**Mechanism of Catalytic Alkane Oxidation by  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ .** On the basis of our experimental results, a mechanism for catalytic alkane oxidation by  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}/\text{ROOH}$  is proposed (eqs 6–8). The first step is rate-limiting O-atom transfer from ROOH to  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  to generate a manganese(VII) nitrido oxo active species,  $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$ , which then oxidizes alkanes ( $\text{R}'\text{H}$ ) via a H-atom abstraction/O-rebound mechanism that is commonly accepted for C–H activation by cytochrome P450 and various metal oxo species.<sup>20–22</sup> The alcohol can be further oxidized to give the corresponding ketone.

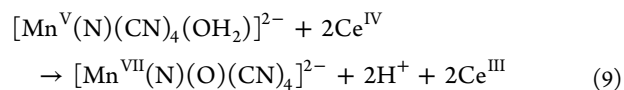


The rates of oxidation of the various alkanes shown in Table 1 were found to be similar. Also, the rate of oxidation of  $\text{C}_6\text{H}_{12}$  is the same as that of  $\text{C}_6\text{D}_{12}$  and is independent of  $[\text{cyclohexane}]$ . However, when an equimolar mixture of  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{D}_{12}$  was used as substrate, there were less deuterated products formed;  $\text{KIE} = [\text{C}_6\text{H}_{11}\text{OH} + \text{C}_6\text{H}_{10}\text{O}]/[\text{C}_6\text{D}_{11}\text{OH} + \text{C}_6\text{D}_{10}\text{O}] = 3.1$ . These results suggest that  $k_6 \ll k_7 \ll k_8$ ; i.e. the rate limiting step is the formation of the active intermediate,  $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$ . The observed similar KIEs for cyclohexane oxidation by  $\text{H}_2\text{O}_2$  and Ce(IV) is in accordance with a common active intermediate. The use of Ce(IV) to generate a metal oxo species from a low-valent aqua complex by proton-coupled electron transfer is well documented (eq 9).<sup>23</sup> Since catalytic oxidation by

Scheme 1. Potential Energy Surfaces for the Oxidation of Cyclohexane by  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}/\text{H}_2\text{O}_2$  at the B3LYP Level in  $\text{CF}_3\text{CH}_2\text{OH}$  SolventScheme 2. Structures of Intermediates and Transition States at the B3LYP Level in  $\text{CF}_3\text{CH}_2\text{OH}$  Solvent<sup>a</sup>

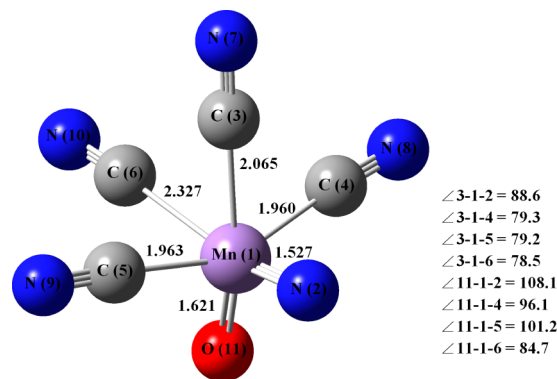
<sup>a</sup>The nitrido ligand is in axial position and *cis* to the oxo ligand.

Ce(IV) was carried out in  $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$  (7:3 v/v), the  $\text{Mn}^{\text{V}}$  probably exists as an aqua species, which can be oxidized by Ce(IV) to generate the  $\text{Mn}^{\text{VII}}=\text{O}$  active intermediate according to eq 9.



**DFT Calculations.** In order to gain more insight into the mechanism of alkane oxidation, DFT calculations have been performed. The potential energy surface for the  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  catalyzed oxidation of cyclohexane with  $\text{H}_2\text{O}_2$  in  $\text{CF}_3\text{CH}_2\text{OH}$  (TFE) is shown in Scheme 1, and the structures of the intermediates and transition states are shown in Scheme 2.  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  first binds with one  $\text{H}_2\text{O}_2$  and two TFE molecules to form  $[\text{Mn}(\text{N})(\text{CN})_4 \cdot (\text{H}_2\text{O}_2) \cdot 2\text{TFE}]^{2-}$  (INT1), which is stabilized by intermolecular hydrogen bonding. In INT1,  $\text{H}_2\text{O}_2$  is *cis* to the nitrido ligand. INT1 then undergoes a 1,2-proton shift to form  $[\text{Mn}(\text{N})(\text{CN})_4 \cdot (\text{O}-\text{OH}_2) \cdot 2\text{TFE}]^{2-}$  (INT4) with assistance from TFE molecules in three sequential steps: (i) INT2,  $[\text{Mn}(\text{N})(\text{CN})_3(\text{CNH})(\text{OOH}) \cdot 2\text{TFE}]^{2-}$ , is formed by a series of proton transfer relays from  $\text{H}_2\text{O}_2$  to adjacent TFE(1) to TFE(2) to cyanide ligand via TS1 with a barrier height ( $\Delta G_{298}^\ddagger$ ) of 14.7 kcal mol<sup>-1</sup>. A short O...H hydrogen bonding (distance  $\approx 1.547$  Å) is found between O(1) of the hydroperoxo ligand (MnOOH) and TFE(1) in INT2; (ii) rearrangement occurs so that the proton in TFE(1) is now coordinated to the O(2) atom in MnOOH via TS2 ( $\Delta G_{298}^\ddagger = 6.5$  kcal mol<sup>-1</sup> relative to INT2) and form  $[\text{Mn}(\text{N})(\text{CN})_4(\text{H}) \cdot (\text{O}-\text{OH}) \cdot 2\text{TFE}]^{2-}$  (INT3), and the MnOOH...CN hydrogen bond is broken; (iii) a series of proton relays occurs from CN to TFE(2) to TFE(1) to O(2) atom in MnOOH and forms INT4 via TS3 ( $\Delta G_{298}^\ddagger = 8.6$  kcal mol<sup>-1</sup> relative to INT3). The O–O in the oxywater ligand in INT4 elongates and eventually a Mn(VII) nitrido oxo complex,  $[\text{Mn}(\text{N})(\text{O})(\text{CN})_4 \cdot (\text{H}_2\text{O}) \cdot 2\text{TFE}]^{2-}$  (INT5) is formed via TS4 ( $\Delta G_{298}^\ddagger = 26.1$  kcal mol<sup>-1</sup>). The formation of INT5 is accompanied by a large release of Gibbs free energy ( $\approx 25$  kcal mol<sup>-1</sup> relative to INT4). The Mn(VII) oxo ligand in INT5 then abstracts a H-atom from cyclohexane followed by O-rebound to give  $[\text{Mn}(\text{N})(\text{CN})_4 \cdot (\text{C}_6\text{H}_{11}\text{OH}) \cdot (\text{H}_2\text{O}) \cdot 2\text{TFE}]^{2-}$  (INT6) via TS5 ( $\Delta G_{298}^\ddagger = 17.2$  kcal mol<sup>-1</sup>). Since there is only one TS in this process, the O-rebound step is probably barrierless. The weakly bound cyclohexanol is then released from INT6 to yield  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ ,  $\text{C}_6\text{H}_{11}\text{OH}$ ,  $\text{H}_2\text{O}$ , and 2TFE.

Natural bond orbital (NBO)<sup>16</sup> charge analysis has been carried out on INT3, TS4, and INT4 (Table S4 and Scheme S1, Supporting Information), which shows that the O(12) bears more negative charge than the O(11). The polarization of the O(12)–O(11) bond in INT4 favors heterolytic bond cleavage and forms INT5 via TS4. NBO has also been carried out on  $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$  (INT5) (Figure 4 and Table S6). In the optimized structure of INT5, the Mn=O distance of 1.621 Å is slightly shorter than those of  $\text{KMn}^{\text{VII}}\text{O}_4$  (av. 1.659 Å),<sup>24</sup> while the



**Figure 4.** Optimized structure of  $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$  (INT5) in solvent at the B3LYP level (bond lengths are in Å).

$\text{Mn}\equiv\text{N}$  bond length of 1.527 Å is slightly longer than that of  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$  (1.507(2) Å).<sup>7</sup>

The possibility of alternative reaction mechanisms has also been explored. For example, attempts were made but failed to (i) locate TS structure for direct O atom abstraction by cyclohexane from INT4 to form INT6; (ii) locate TS structure for 1,2-proton shift when there is only one TFE bonded with  $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$  and  $\text{H}_2\text{O}_2$  in INT2. Also H-atom abstraction from cyclohexane by the nitrido ligand in INT5 is not feasible as the barrier height ( $\Delta G_{298}^\ddagger = 31.2$  kcal mol<sup>-1</sup>) is significantly higher.

**Concluding Remarks.** In conclusion, we have demonstrated that  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$  is a highly efficient catalyst for the oxidation of alkanes by various oxidants. Unprecedented yields of >95% are obtained for  $\text{H}_2\text{O}_2$  at room temperature. As far as we are aware, this is also the first example of manganese catalyzed alkane oxidation using Ce(IV) as the oxidant and  $\text{H}_2\text{O}$  as the oxygen source, with yields >80%. We provide experimental evidence that the active intermediate in oxidation by ROOH and Ce(IV) is a Mn(VII) nitrido oxo species,  $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$ , which is also supported by DFT calculations. The catalytic alkane oxidation activity of  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$  is much higher in  $\text{CF}_3\text{CH}_2\text{OH}$  solvent than in  $\text{CH}_3\text{CN}$ .  $\text{CF}_3\text{CH}_2\text{OH}$  may help to stabilize the  $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4(\text{ROOH})]^{2-}$  intermediate by H-bonding, as supported by DFT calculations. This H-bonding could also facilitate heterolytic O–O cleavage to generate the  $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$  active species, as well as subsequent H-atom abstraction/O-rebound with alkane. H-bonding between  $\text{CF}_3\text{CH}_2\text{OH}$  and cyanide was also observed experimentally by solution IR spectroscopy. When  $\text{CF}_3\text{CH}_2\text{OH}$  (4 vol %) was added to the Mn(V) catalyst in  $\text{CH}_2\text{Cl}_2$ , the peak at 2116 cm<sup>-1</sup> shifted to 2127 cm<sup>-1</sup> (Figure S11, Supporting Information). Our results suggest that  $\text{Mn}^{\text{V}}\equiv\text{N}$  is potentially a new and useful platform for the construction of highly efficient oxidation catalysts.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details, ESI/MS, and DFT data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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