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## Characterization and Reactivity of a Tetrahedral Copper(II)-Alkylperoxido Complex

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Abstract: tetrahedral Cu<sup>II</sup>-alkylperoxido Α complex  $[Cu^{II}(TMG_{3}tach)(OOCm)]^{+}$  (1<sup>00Cm</sup>) (TMG\_{3}tach = {2,2',2''-[(1s,3s,5s)cyclohexane-1,3,5-triyl]tris-(1,1,3,3-tetramethyl quanidine)}. OOCm = cumyl peroxide) is prepared and characterized by UV-vis, CSI-mass, resonance Raman, and EPR spectroscopic methods. Product analysis of the self-decomposition reaction of  $\mathbf{1}^{oocm}$  in acetonitrile (MeCN) indicates that the reaction involves O-O bond homolytic cleavage of the peroxide moiety with concomitant C-H bond activation of the solvent molecule. When an external substrate such as 1,4-cyclohexadiene (CHD) is added, the O-O bond homolysis leads to C-H activation of the substrate. Furthermore, the reaction of 1<sup>oocm</sup> with 2,6-di-tert-butylphenol derivatives produces the corresponding phenoxyl radical species (ArO•) together with a Culcomplex via a concerted proton-electron transfer (CPET) mechanism. Details of the reaction mechanisms are explored by DFT calculations.

#### Introduction

Transition-metal alkylperoxide complexes (M<sup>n+</sup>-OOR) have long been attracting much attention as important active oxygen-based intermediates in biological and catalytic oxidation/oxygenation reactions.  $^{[1]\,[1]\,[1]\,[1]\,[1]}$  The O–O bond cleavage in  $M^{n+}\text{-}OOR$ species is an important pathway in the generation of high-valent metal-oxido complexes, which are the key reactive intermediates in catalytic oxidation/oxygenation reactions. Most of the extensively studied iron(III)-alkylperoxido complexes are supported by mixed pyridyl-alkylamine ligands and undergo homolytic O-O bond cleavage to generate an iron(IV)-oxido species (Fe<sup>IV</sup>=O).<sup>[2]</sup> On the other hand, less was known about the intrinsic reactivity of Cull-alkylperoxido complexes.<sup>[3]</sup> We have recently examined the reactivity of some Cu<sup>II</sup>-alkylperoxido complexes that undergo O-O bond homolytic cleavage to induce

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intra- and intermolecular substrate oxidation reactions.<sup>[4]</sup> These studies have provided important insights into the catalytic mechanism of copper monooxygenases with a mononuclear copper reaction center, where a Cu<sup>II</sup>-oxyl radical species (Cu<sup>II</sup>– O•), generated via O–O bond homolysis of a peroxido precursor, is considered as a key reactive intermediate for the aliphatic C–H bond hydroxylation of substrates.<sup>[5]</sup>

Here, we examine the reactivity of a mononuclear Cu<sup>II</sup>-cumyl peroxido complex  $1^{00Cm}$  having a tetrahedral geometry, which is supported by our recently introduced tridentate ligand TMG<sub>3</sub>tach {2,2',2''-[(1s,3s,5s)-cyclohexane-1,3,5-triyl]tris-(1,1,3,3-

tetramethyl guanidine)} (Figure 1).<sup>[6]</sup> The relatively rigid and bulky TMG<sub>3</sub>tach ligand imposes an unusual tetrahedral geometry to Cu<sup>II</sup>, making it possible to mimic the reaction center of some mononuclear copper monooxygenases such as dopamine- $\beta$ -monooxygenases (D $\beta$ M) and peptidylglycine  $\alpha$ -hydroxylating monooxygenase (PHM). As an extension of the seminal work by Kitajima and coworkers,<sup>[7]</sup> reaction of 1<sup>00Cm</sup> with 1,4-cyclohexadiene (CHD) and substituted phenols (ArOH) have been examined to elucidate the reactivity of such a tetrahedral copper(II)-alkylperoxido complex.



Figure 1. Structure of 1<sup>00Cm</sup>

#### **Results and Discussion**

#### Generation and Characterization of the Copper(II)alkylperoxido Complex

In our previous study,<sup>[6]</sup> it was demonstrated that the tetrahedral copper(II)-bromide complex of TMG<sub>3</sub>tach  $1^{Br}$  undergoes ligand exchange reaction with methanol in the presence of a base to give the methoxide complex  $1^{OMe}$  also having a tetrahedral structure (Scheme 1).



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In this study, the methoxide complex  $1^{OMe}$  was further converted to the copper(II)-cumylperoxido complex  $1^{OOCm}$  by ligand exchange reaction of the methoxide ligand with cumene hydroperoxide (Scheme 1). The spectroscopic features and reactivity of  $1^{OOCm}$  are compared to those of the previously reported copper(II)-cumylperoxido complexes  $2^{OOCm}$  and  $3^{OOCm}$ supported by tridentate ligand bpa [*N*,*N*-bis(2pyridylmethyl)benzylamine] and tetradentate ligand tpa [tris(2pyridylmethyl)amine], having a square planer and a trigonal bipyramidal structure, respectively (Figure 2).<sup>[4b]</sup>



Figure 2. Structures of 2<sup>00Cm</sup> and 3<sup>00Cm</sup>

Addition of an excess amount of cumene hydroperoxide (R = -C(Me)<sub>2</sub>Ph, CmOOH) to **1**<sup>OMe</sup> at -60 °C in CH<sub>2</sub>Cl<sub>2</sub> resulted in spectral changes shown in Figure 3(A) (red spectrum to blue spectrum). The generated species exhibited LMCT bands at 345 ( $\varepsilon$ = 1850 M<sup>-1</sup> cm<sup>-1</sup>) and 505 nm ( $\varepsilon$ = 2600 M<sup>-1</sup> cm<sup>-1</sup>) together with d-d bands at 735 (320) and 920 nm (280). The positions and relative intensity of the LMCT bands as well as the d-d bands are significantly different among the cumylperoxido complexes (**1**<sup>OOCm</sup>, **2**<sup>OOCm</sup>, and **3**<sup>OOCM</sup>), reflecting their different geometry.<sup>[4b]</sup>

In order to get the maximum intensity of the absorption spectrum, almost three equivalents of CmOOH was required (inset of Figure 3(A)), suggesting that this is an equilibrium reaction. The equilibrium constant  $\mathcal{K}_{eq}$  for the reaction between  $\mathbf{1}^{OMe}$  and CmOOH can be expressed by the slope of the plot of  $(A - A_0)/(A_{\infty} - A)$  against [CmOOH]<sub>0</sub> –  $\alpha$  [Cu]<sub>0</sub> [ $\alpha = (A - A_0)/(A_{\infty} - A_0)$ ], where  $A_0$  and  $A_{\infty}$  are the initial and the final absorptions of the titration and [CmOOH]<sub>0</sub> and [Cu]<sub>0</sub> denote the concentration of the added CmOOH and  $\mathbf{1}^{OMe}$ , respectively.<sup>[8]</sup> The plot gave a straight line passing through the origin as shown in Figure 3(B), from which the  $\mathcal{K}_{eq}$  value was determined as (2.7 ± 0.04) x 10<sup>4</sup> M<sup>-1</sup>.



**Figure 3.** (A) UV-vis spectral change for the reaction of  $[Cu^{II}(TMG_3tach)(OMe)](OTf)$  ( $1^{OMe}$ , 0.25 mM) with CmOOH (5.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> at -60 °C. Inset: The absorption change at 505 nm for the titration of  $1^{OMe}$  (0.25 mM) with CmOOH in CH<sub>2</sub>Cl<sub>2</sub> at -60 °C. (B) Plot of  $(A - A_0)/(A_{\infty} - A)$  vs [CmOOH]<sub>0</sub> –  $\alpha$  [Cu]<sub>0</sub> [ $\alpha = (A - A_0)/(A_{\infty} - A_0)$ ] for formation of  $1^{OOCm}$ .

The resulting species was stable below  $-40 \,^{\circ}$ C, but gradually decomposed at higher temperature to re-generate  $1^{Br}$ , which was used as the starting material for the generation of  $1^{OMe}$  (Scheme 1). Thus, Br<sup>-</sup> originating from  $1^{Br}$  in the solution rebinds to the copper(II) ion at higher temperature (Scheme 2), indicating higher affinity of Br<sup>-</sup> as compared to the alkylperoxide anion.



Scheme 2. Ligand exchange reactions with copper(II) complexes 1<sup>x</sup>.

In order to prevent such an undesired rebound of Br<sup>-</sup> (Scheme 2), we have developed a method with Br<sup>-</sup>-free conditions for the preparation of the alkylperoxido-complex. Consequently, we have found that the treatment of CmOOH (0.75 mM) with a 1 : 1 mixture of TMG<sub>3</sub>tach (0.25 mM) and [Cu<sup>1</sup>(MeCN)<sub>4</sub>]ClO<sub>4</sub> (0.25 mM) in MeCN at 0 °C gave the same spectrum to that of 1<sup>00Cm</sup> generated from 1<sup>0Me</sup> as shown in Figure S1. Due to the absence of Br<sup>-</sup> in the system, with this approach, 1<sup>00Cm</sup> exhibited higher stability than with the original method, thus allowing us to carry out further characterization by CSI-MS, resonance Raman, and EPR spectroscopies.

The CSI-MS (cold-spray ionization mass spectrum) showed a peak cluster at m/z = 637.39 (Figure 4(A)), the peak position as well as the peak distribution pattern of which was consistent with the molecular formula of the mononuclear Cu<sup>II</sup>-cumylperoxido complex, [Cu<sup>II</sup>(TMG<sub>3</sub>tach)(OOCm)]<sup>+</sup> (1<sup>00Cm</sup>). When the sample was prepared with <sup>18</sup>O-labeled Cm<sup>18</sup>O<sup>18</sup>OH, the peak cluster at m/z = 637.39 shifted by four mass units to 641.39, which further supported the formation of 1<sup>00Cm</sup> (Figure 4(A)).



Figure 4. (A) CSI-MS of  $[Cu<sup>II</sup>(TMG_3tach)(OOCm)]^+$  (1<sup>0ocm</sup>), generated by with Cm<sup>16</sup>O<sup>16</sup>OH (black) and Cm<sup>18</sup>O<sup>18</sup>OH (red) in acetone at -40°C (the simulated spectrum is shown in blue). The whole spectrum is shown in Figure S2(A). (B) Resonance Raman spectra of 1<sup>00Cm</sup> generated with Cm<sup>16</sup>O<sup>16</sup>OH (black) and Cm<sup>18</sup>O<sup>18</sup>OH (red) in MeCN at -20°C, excited at 488 nm (difference spectrum <sup>16</sup>O-<sup>18</sup>O is shown in blue; asterisks denote solvent peaks).

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The resonance Raman spectrum of  $1^{oocm}$  measured with  $\lambda_{ex}$ = 488 nm laser light at -20 °C exhibited multiple Raman bands at 883, 836, 624, 544, 488, and 436 cm<sup>-1</sup>, which shifted to 861, 798, 607, 537, 477, and 428 cm<sup>-1</sup> upon <sup>18</sup>O-substitution using Cm<sup>18</sup>O<sup>18</sup>OH (Figure 3(B)). The existence of the multiple Raman bands is also consistent with the formation of the Cullalkylperoxido complex (1<sup>oocm</sup>).<sup>[9]</sup> The bands in the 800 cm<sup>-1</sup> region can be assigned to the O-O and C-O stretching vibrations of the cumylperoxide moiety, and the band at 624 cm<sup>-1</sup> is due to the Cu-O stretching vibration. The other bands at 544, 488, and 436 cm<sup>-1</sup> can be assigned to C-C-C and O-C-C deformation modes of the alkylperoxide moiety. Both the O-O stretching vibration and the Cu-O stretching vibration energies of 100cm (883 and 624 cm<sup>-1</sup>) are higher than those of 2<sup>00Cm</sup> (864 and 588 cm<sup>-1</sup>) and 3<sup>00Cm</sup> (879 and 607 cm<sup>-1</sup>).<sup>[4b]</sup> Further theoretical studies are needed to understand the reason for such differences.

The EPR spectrum of  $1^{OOCm}$  shows an orthorhombic signal (Figure 5), similar to that of the Cu<sup>II</sup>-methoxido complex  $1^{OMe, [6]}$  suggesting that  $1^{OOCm}$  also has a tetrahedral geometry. Spin quantification of this spectrum indicates that 96% of the Cu<sup>II</sup> species exists in the sample, indicating nearly quantitative formation of  $1^{OOCm}$ .



Figure 5. X-band (9.011 GHz) EPR spectrum of  $1^{oocm}$  in  $CH_2Cl_2$  at 77 K (black) and its simulation (red).

To clarify the formation mechanism of  $1^{oocm}$  from the Culcomplex and CmOOH, product analysis was carried out by using HPLC. When 3.0 equiv of CmOOH with respect to the Cu<sup>I</sup> complex were added, nearly 0.5 equiv of CmOH (cumyl alcohol) were formed immediately after the generation of  $1^{oocm}$  (quenched at low temperature; 0°C). We previously reported that the reaction of Cu<sup>I</sup> complexes and 0.5 equiv of CmOOH gives a  $\mu$ hydroxido- $\mu$ -alkoxidodicopper(II) species through a heterolytic O-O bond cleavage of the Cu<sup>I</sup>-alkylperoxido complex (Scheme 3).<sup>[10]</sup> A similar type intermediate may be formed in the reaction of the Cu<sup>I</sup> complex of TMG<sub>3</sub>tach and 0.5 equiv of CmOOH, which then reacts with another equiv of CmOOH to give  $1^{oocm}$  (Scheme 3).



Scheme 3. Generation of 1<sup>00Cm</sup> by the reaction of [Cu<sup>I</sup>(L)] and CmOOH.

Reactivity of 1<sup>00Cm</sup>

Self-decomposition. The Cu<sup>II</sup>-alkylperoxido complex 1<sup>oocm</sup> is relatively stable below 0°C, but it gradually decomposed at

higher temperature following first-order kinetics as shown in Figure 6(A);  $k_{dec} = 5.2 \times 10^{-2} \text{ s}^{-1}$  at 60°C (the first-order plot is shown in the inset). From the temperature-dependence of  $k_{dec}$ , activation parameters are obtained as  $\Delta H^{\ddagger} = 83.3 \pm 3.8 \text{ kJ mol}^{-1}$ and  $\Delta S^{\ddagger} = -39.4 \pm 2.8 \text{ J K}^{-1} \text{ mol}^{-1}$  (Figure 6(B)).<sup>[11]</sup> After the decomposition of 1<sup>oocm</sup> in MeCN, the CSI-MS of the solution showed a peak cluster at m/z = 512.32, which indicates formation of a Cu<sup>II</sup>-cyanido complex, [Cu<sup>II</sup>(TMG<sub>3</sub>tach)(CN)]<sup>+</sup> (1<sup>CN</sup>) (Figure S2(B)). Analysis of the organic products by HPLC indicates that 2.3 equiv of PhC(O)Me (acetophenone) and 0.6 equiv of CmOH (cumyl alcohol) are formed from the 3.0 equiv of CmOOH initially added (see above). Since 0.5 equiv of CmOH is generated for the formation of 100cm from the Cul complex and CmOOH (Scheme 3), the amount of CmOH formed from the selfdecomposition reaction is only 0.1 equiv. Thus, the main decomposition product is PhC(O)Me, suggesting that the selfdecomposition primarily involves homolytic O-O bond cleavage of the peroxide moiety of 1<sup>oocm</sup>, as reported in our previous paper.[4b]



**Figure 6.** (A) UV-vis spectral change for the decomposition of  $1^{00Cm}$  (0.25 mM) in MeCN at 60°C. Inset: first-order plot based on the absorption change at 515 nm. (B) Eyring plot for the decomposition of  $1^{00Cm}$  in MeCN.

**C–H Bond Activation of External Substrates**. Addition of an excess amount of 1,4-cyclohexadiene (CHD) to a MeCN solution of 1<sup>oocm</sup> at 30°C significantly accelerates the first-order decay rate of 1<sup>oocm</sup> as shown in Figure 7. From the plot of pseudo-first-order rate constants ( $k_{obs}$ ) against the concentration of CHD, the second-order rate constant ( $k_2$ ) was determined from the slope as  $(2.3 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  (Figure 7(B)). The intercept of the plot ( $(2.6 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ ) was nearly identical to that of the self-decomposition rate ( $2.5 \times 10^{-4} \text{ s}^{-1}$ ), estimated from extrapolation of the Eyring plot for self-decomposition at 30°C (Figure 6(B)).





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From the final reaction mixture, 2.0 equiv of CmOH was detected by HPLC together with 1.0 equiv of Ph(O)Me, where all CmOOH (3.0 equiv added initially) was consumed. In this case as well, 0.5 equiv of CmOH was formed from the formation of  $1^{OOCm}$  (Scheme 3). Thus, 1.5 equiv of CmOH was formed from the reaction of  $1^{OOCm}$  with CHD, indicating that CmOH became the major product in contrast to the case of the self-decomposition reaction.

The results can be interpreted by the reaction mechanism shown in Scheme 4. Hydrogen atom abstraction from CHD by 1<sup>oocm</sup> proceeds via concomitant O-O bond homolysis of the alkylperoxido moiety, which generates Cu<sup>ll</sup>-OH, a CHD radical, and CmO• (step 1). The first-order dependence of the reaction on the CHD concentration (Figure 7(B)) unambiguously demonstrates the direct reaction between 1<sup>oocm</sup> and CHD. The formed CmO• may also abstract a hydrogen atom from the CHD radical intermediate to give CmOH and benzene as a product (step 2, major pathway). As a minor pathway, CmO• undergoes B-scission of Me• to form PhC(O)Me (step 3). The alternative O-O bond cleavage pathway of 1<sup>oocm</sup>, generating a Cu<sup>II</sup>–O• species is less likely based on the high instability of the metal-oxyl species.<sup>[12]</sup>

In the self-decomposition of  $1^{oocm}$  in the absence of substrate (CHD),  $1^{oocm}$  may also abstract a hydrogen atom from the solvent molecule (MeCN) in a similar manner, generating Cu<sup>II</sup>OH, CmO•, and •CH<sub>2</sub>CN (Scheme S1). Rebound of CmO• to •CH<sub>2</sub>CN gives CmOCH<sub>2</sub>CN, from which CmOH, HCHO, and HCN are generated by hydrolysis (Scheme S1). However, such a radical rebound reaction may be entropically unfavorable, so that the self-decomposition of CmO• ( $\beta$ -scission) occurs predominantly to give PhC(O)Me, as experimentally observed (see above).

Regarding to the Cu<sup>II</sup> complex in the presence of CHD, the generated Cu<sup>II</sup>OH species reacts with CmOOH to regenerate 1<sup>oocm</sup> that undergoes the same reaction with the CHD substrate until all CmOOH is consumed; thus, the reaction is catalytic. In the absence of substrate, the generated Cu<sup>II</sup>OH may be trapped by HCN to give the Cu<sup>II</sup>-CN complex, as confirmed by CSI-MS (Figure S2(B)).<sup>[13]</sup>



Scheme 4. Reaction mechanism for the reaction of 100Cm and CHD.

To examine the electronic effects on the reactivity of the Cu<sup>II</sup>cumylperoxido complex, the 4-methyl-cumylperoxido and 4bromo-cumylperoxido derivatives ( $1^{OOCm(Me)}$  and  $1^{OOCm(Br)}$ ) were also prepared. The UV-vis spectra showed blue-shifts of the LMCT band with increasing electron-withdrawing nature of the *p*substituents;  $1^{OOCm(Br)}$ : 500 nm,  $1^{OOCm}$ : 505 nm,  $1^{OOCm(Me)}$ : 512 nm (Figure S3). The cumylperoxide complexes oxidized CHD with the pseudo-first-order rate constant ( $k_{obs}$ ) slightly increasing in the order of  $1^{OOCm(Br)}$  ((1.4 ± 0.1) ×  $10^{-2}$  M<sup>-1</sup> s<sup>-1</sup>) <  $1^{OOCm}$  ((2.3 ± 0.1) ×  $10^{-2}$  M<sup>-1</sup> s<sup>-1</sup>) <  $1^{OOCm}$  ((2.3 ± 0.2) ×  $10^{-2}$  M<sup>-1</sup> s<sup>-1</sup>, Figure S4). These results are consistent with the O–O bond homolytic cleavage mechanism, since the electron-donating substituent tends to decrease the bond dissociation energy of the O–O bond.<sup>[14]</sup>

Density functional theory (DFT)<sup>[15]</sup> was used to gain insights into the structural and energetic details associated with the steps involved in the mechanism. The alkylperoxide is stabilized by weak hydrogen bonding of both oxygen atoms to the 1,1,3,3tetramethyl guanidine methyl groups, which is confirmed by a QTAIM analysis (see Figure S12).<sup>[16]</sup> Figure 8 shows the potential energy surface for the reaction of 1<sup>00Cm</sup> with CHD. The first step in the reaction with CHD involves a concerted mechanism consisting of the H-atom transfer from CHD to O1 (oxygen atom coordinated to the Cu center) and the O-O bond homolytic cleavage of the peroxido mojety. The associated free energy of activation (TS1) is 120.5 kJ mol<sup>-1</sup>, in agreement with our earlier report.<sup>[4]</sup> The Cu–O1 bond is significantly elongated (2.033Å in TS1 vs. 1.881Å in 1<sup>00Cm</sup>), while the O-O bond is apparently weakened due to the H atom migration (1.465 Å in TS1 vs. 1.417Å in 1<sup>00Cm</sup>; C--H (1.335Å) and O--H (1.258Å) in **TS1**) (Figure S13). This confirms that the reaction proceeds in a concerted fashion as mentioned above. CmO• abstracts a hydrogen atom from the generated CHD radical intermediate with a small activation energy (26.9 kJ mol-1) to give CmOH (TS2), leading to the thermodynamically favored major product (-120.8 kJ mol-1). Alternatively, CmO• could react with the CHD substrate to form another equiv of the CHD radical intermediate via TS2'. However, this step is unlikely to occur due to a significantly higher barrier (80.9 kJ mol<sup>-1</sup>). The  $\beta$  scission of Me• producing acetophenone requires a barrier of 36.7 kJ mol-1 (TS3), which is larger than that of TS2 (26.9 kJ mol<sup>-1</sup>). Thus, the formation of CmOH becomes the major pathway as experimentally observed.



Figure 8. B3LYP-D3 computed potential energy surface for the reaction of 1°°Cm with CHD ( $\Delta G$  in kJ mol<sup>-1</sup>).

The reactivity of  $1^{00Cm}$  toward CHD ( $k_2 = (2.3 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ) is slightly lower than that of  $2^{00Cm}$  (4.9 x  $10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ), even though the O–O bond strength between  $1^{00Cm}$  and  $2^{00Cm}$  is significantly different (883 cm<sup>-1</sup> and 864 cm<sup>-1</sup>, respectively).<sup>[4b]</sup> Furthermore, the reactivity of  $1^{00Cm}$  is much higher than that of  $3^{00Cm}$  (7.9 x  $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>[4b]</sup> even though the O–O bond of the

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former is stronger than that of the latter (879 cm<sup>-1</sup>). These results may be due to a geometric effect on the reactivity of Cu<sup>II</sup>-alkylperoxido complexes toward CHD. Namely, the unusual tetrahedral Cu<sup>II</sup>-complex is essentially more reactive as compared to the Cu<sup>II</sup>-complex having ordinary square planer and trigonal bipyramidal structure.

**Phenol Oxidation**. The reaction of  $1^{00Cm}$  toward phenol derivatives was also examined. Addition of an excess amount of 2,4,6-tri-*tert*-butylphenol (ArOH) to a MeCN solution of  $1^{00Cm}$  at 0°C resulted in the spectral change shown in Figure 9(A), in which formation of the corresponding phenoxyl radical species is apparent at around 400 nm with the characteristic fine structures. Based on the molar absorption coefficient of ArO• at  $\lambda_{max} = 630$  ( $\varepsilon = 400 \pm 10 \ M^{-1} \ cm^{-1}$ ),<sup>[17]</sup> the yield of the phenoxyl radical was estimated as ca. 100 % based on  $1^{00Cm}$ .



Figure 9. (A) UV-vis spectral change for the reaction of  $1^{00Cm}$  (0.25 mM) with 2,4,6-tri-*tert*-butylphenol (7.5 mM) in MeCN at 0°C. Inset: first-order plot based on the absorption change at 505 nm. (B) Plot of  $k_{obs}$  vs substrate concentration.

The second-order rate constant  $k_2$  was then determined as  $(3.3 \pm 0.2) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$  from the slope of a linear plot of firstorder rate constants  $k_{obs}$  against the phenol concentrations (Figure 9(B)). The EPR spectrum of the final reaction mixture gave a signal due to the corresponding phenoxyl radical species at g = 2.0048 but no Cu<sup>II</sup> species (Figure S5), indicating that  $1^{OOCm}$  was reduced to a Cu<sup>II</sup> complex.

In this reaction as well, 3.0 equiv of CmOOH was used for the quantitative formation of  $1^{00Cm}$ . In this case, the product yields of CmOH and PhC(O)Me were 0.7 equiv and 0.6 equiv based on the copper complex, respectively, where 0.5 equiv of CmOH was generated during the formation of  $1^{00Cm}$  from the Cu<sup>1</sup> complex (Scheme 3). Thus, the amount of CmOH generated from the reaction with the phenol substrate was only 0.2 equiv. It should also be noted that about 1.5 equiv of CmOOH (starting material) was recovered from the final reaction mixture.

To examine the electronic effects of the *p*-substituent (X), reactions with a series of *para*-substituted 2,6-di-*tert*-butylphenol derivatives were examined (X = -<sup>t</sup>Bu, -Me, -H, -CONHMe, -COOMe, and -COMe; Figure 9 and Figures S6-S10). Notably, a plot of log  $k_2$  against the Hammett constant  $\sigma_p$  gave a linear correlation with a positive Hammett  $\rho$  value of 3.0 (Figure 10). Such a positive Hammett  $\rho$  value is indicative of a formally nucleophilic character of the Cu<sup>II</sup>-alkylperoxido complex 1<sup>oocm</sup>. The reaction of 1<sup>oocm</sup> with 4-substituted 2,6-di-*tert*-butylphenol derivatives (ArOH) may involve proton-transfer (PT) together with electron-transfer (ET) to give Cu<sup>I</sup>-complex (LCu<sup>I</sup>), phenoxyl radical (ArO•), and CmOOH (starting material). Thus, the reaction

can be regarded as a concerted proton/electron transfer (CPET) reaction (Scheme 5). The generation of acetophenone suggests that the O–O bond cleavage may also occur as a minor pathway. In the reaction with less bulky phenols such as *p*-methoxy-phenol and pentafluorophenol, the generated Cu<sup>1</sup> complex (LCu<sup>1</sup>) immediately reacted with the generated phenoxyl radical (ArO•) to form the corresponding Cu<sup>II</sup>-phenolato complex (LCu<sup>II</sup>OAr) (Figure S11).



Figure 10. Hammett plot for the reaction of 1<sup>00Cm</sup> (0.25 mM) and 4-substitute-2,6-di-*tert*-butylphenol derivatives in MeCN at 0°C. Kinetic analysis data are presented in Figures S8 and S10-S14.



Scheme 5. Reaction of 1<sup>00Cm</sup> with phenol derivatives.

DFT calculations show that the proton transfer from the phenol to  $1^{oocm}$  takes place along with the Cu–O bond dissociation, leading to electron transfer with a barrier of 67.1 kJ mol<sup>-1</sup>, producing the Cu<sup>I</sup> complex (LCu<sup>I</sup>) and the phenoxyl radical product (ArO•) (Figure 11). The O–H bond distances of ArO--H and CmOO---H in **TS1** are 1.197Å and 1.224Å, respectively, whereas the Cu–O bond is elongated (2.038Å) as shown in Figure S15. The spin density of Cu and the phenol oxygen remain almost the same (Figure S16), indicating that the reaction proceeds in a concerted manner. Thus, these DFT results confirm that the reaction of  $1^{oocm}$  with phenol derivatives follows a CPET mechanism.<sup>[18]</sup>



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#### Conclusions

A Cu<sup>II</sup>-alkylperoxide complex 1<sup>oocm</sup> exhibiting an unusual tetrahedral geometry has been prepared and characterized by several spectroscopic methods. 1<sup>oocm</sup> is demonstrated to exhibit C–H and O–H bond activation reactivity towards CHD and ArOH substrates, respectively. In the reaction with CHD, direct hydrogen atom abstraction from CHD and O–O bond cleavage of 1<sup>oocm</sup> occur in a concerted manner (Figure 8). Comparison of the reactivity among the Cu<sup>II</sup>-OOCm complexes (1<sup>oocm</sup>, 2<sup>ooCm</sup>, and 3<sup>oocm</sup>) suggests that the unusual tetrahedral Cu<sup>II</sup>-complex is more reactive as compared to the Cu<sup>II</sup>-complex having ordinary square planer and trigonal bipyramidal structure. On the other hand, the oxidation of phenols by 1<sup>oocm</sup> is shown to involve a CPET mechanism (Figure 11). These results provide important new insights into the reactivity of bioinspired Cu<sup>II</sup>-peroxido complexes.

#### **Experimental Section**

General. The reagents and the solvents used in this study, except the ligand, cumene hydroperoxide derivatives and the copper complexes, were commercial products of the highest available purity and used as received without further purification, unless otherwise noted. Ligand TMG<sub>3</sub>tach and its copper(II)bromide complex ([Cu<sup>II</sup>(TMG3tach)(Br)](OTf) (1<sup>Br</sup>) were obtained from the previous study.<sup>[6]</sup> Cumene hydroperoxide derivatives (Cm<sup>(X)</sup>OOH, Cm<sup>(X)</sup> = - $C(Me)_2C_6H_4$ -p-X; X = Me, H, Br) used in this study were prepared by the reported procedure, and purified by silica gel column chromatography (eluent: ether).<sup>[19]</sup> <sup>18</sup>O-labeled cumene hydroperoxide (Cm<sup>18</sup>O<sup>18</sup>OH) was prepared using <sup>18</sup>O<sub>2</sub> instead of <sup>16</sup>O<sub>2</sub> by the same procedure. All reactions were carried out under N<sub>2</sub> atmosphere using standard Schlenk techniques or a glovebox (a KK-011-AS, KOREA KIYON product). UV-visible spectra were taken on a Jasco V-570 or a Hawlett Packard 8453 photo diode array spectrophotometer equipped with a Unisoku thermostated cryostat cell holder USP-203. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a JEOL ECP400 or a JEOL ECS400. Elemental analyses were performed on a Yanaco New Science Inc. CHN order MT-5 or a J-SCIENCE LAB Co., Ltd. MICRO CORDER JM10. EPR measurements were carried out on a JEOL JES-TE200, and g values are determined based on the signal of an Mn<sup>II</sup> marker. EPR spectra were simulated with EPR simulation software, SpinCount, distributed by Prof. M. Hendrich. CSI-MS (coldelectrospray ionization mass spectrum) measurements were performed on a BRUKER cryospray micrOTOF II.

**Resonance Raman Spectroscopy.** Resonance Raman scattering was excited at 488 nm from an Ar laser (NEC, GLG3200). Resonance Raman scattering was dispersed by a single polychromator (Ritsu Oyo Kogaku, MS-100DG) and was detected by a liquid nitrogen cooled CCD detector (HORIBA JOBIN YVON, Symphony CCD-1024 × 256-OPEN-1LS). The resonance Raman measurements were carried out using a rotating NMR tube (outer diameter = 5 mm) thermostated at –20 °C by flashing cold nitrogen gas. A 135° back scattering geometry was used. A 1.2 mM solution of 1<sup>oocm</sup> in MeCN was prepared in an NMR tube placed in an ice bath. For the preparation, CmOOH in MeCN was added to the complex solution via a Hamiltonian micro syringe.

**Computational Details.** All DFT calculations were performed using the Gaussian 09 suite of programs.<sup>[20]</sup> The geometries were optimized using the B3LYP-D3 functional with LACVP basis set comprising the LanL2DZ-Los Alamos effective core potential for Cu<sup>[21]</sup> and a 6-31g(d) basis set<sup>[22]</sup> for the other atoms (carbon, nitrogen, oxygen and hydrogen) (B-I).<sup>[23]</sup> Single point calculations were performed using a def2-TZVP basis set<sup>[15, 24]</sup> (B-II) on the optimized geometries. This functional has been employed by us and others

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earlier to predict the correct spin state energetic of several mononuclear metal complexes. Frequency calculation on the optimized structures was undertaken to confirm the minima on the potential-energy surface (PES) and also to obtain free energy and zero-point energy corrections. The solvation energies were computed by using polarizable continuum model (PCM) solvation model where acetonitrile has been used as the solvent. All reported energies are B3LYP-D3 gas-phase energies incorporating free energy corrections (at B-I level) at 298.15 K, unless otherwise mentioned. Although the inclusion of solvent in the optimization to a certain extent, the trend for the computed energetics are similar. Therefore, here we have performed only a single point calculation including solvation using the PCM model. Additionally, for comparison, we have also given the zero-point energy (ZPE) corrected values in both gas-phase and solvent phase in the ESI. The natural bond orbital analysis and Wiberg indices were obtained by using the NBO6 program. The wave function for the use in quantum theory of atoms in molecules (QTAIM) analysis<sup>[25]</sup> were generated from single point calculation using B3LYP/def2-TZVP level as implemented in the Gaussian 09 and the QTAIM calculations are performed using AIM2000 package.<sup>[25]</sup> Molecular orbital and Natural bond orbital (NBO) analysis<sup>[26]</sup> were performed using G09 suite.[20]

Kinetic Measurements. Kinetic measurements for the reaction of copper(II) alkylperoxide complex [Cu<sup>II</sup>(TMG<sub>3</sub>tach)(OOCm(X))](ClO<sub>4</sub>) (1<sup>oocm(X)</sup>) were performed using a Hawlett Packard 8453 photo diode array spectrophotometer equipped with a Unisoku thermostated cryostat cell holder USP-203 (a desired temperature can be fixed within ± 0.5 °C) in MeCN at 0 °C. 1<sup>oocm(X)</sup> was generated by adding a cumylperoxide derivative (0.75 mM, in MeCN) into a solution of the copper(I) complex, generated in situ by mixing [Cu<sup>I</sup>(MeCN)<sub>4</sub>](ClO<sub>4</sub>) (0.25 mM) and TMG<sub>3</sub>tach (0.25 mM), in a UV cell (1.0 cm path length) through a silicon rubber cap by using a micro syringe. Increase of the absorption bands (505 nm) due to  $1^{\text{oocm}(X)}$  was monitored to confirm its formation. An excess amount of substrate (10-50 equiv to the copper complex) was then introduced to the solution of 100cm(X), and the reaction was followed by monitoring the decrease of the absorption bands. The pseudo-first-order rate constants for the reaction were determined from the plots of  $\ln(\Delta A)$  vs time based on the time course of the absorption change at  $\lambda_{max}$  due to  $1^{oocm(X)}$ . The second-order rate constants for the faster reactions were determined from the slopes of the plot  $(A-A_0)/([Cu \text{ complex}]_0(A-A_\infty))$  vs time based on the time course of the absorption change at  $\lambda_{max}$  due to  $1^{oocm(x)}$  for the 1 : 1 reaction between 100Cm(X) and the substrate.

**Product Analysis.** Decomposition products derived from cumene hydroperoxide and oxidation products of the substrates were analyzed by using a HPLC system consisting of a Shimadzu LC-6A chromatographic pump and an on-line Shimadzu UV-vis spectrophotometric detector. Reverse phase chromatography was performed on an ODS column (Cosmosil 5C18 -AR-II, 250 mm x 4.6 mm, Nakarai Tesque) at room temperature with an acetonitrile-water (40:60) mixed solvent as mobile phase at a constant flow rate of 0.5 mL min<sup>-1</sup>. The yields of products were determined by comparing the integrated peak areas of the products with that of the internal standard (anisole) using calibration lines.

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## **FULL PAPER**

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## **FULL PAPER**

#### **Entry for the Table of Contents**

#### FULL PAPER

A Cu<sup>II</sup>-alkylperoxido complex exhibiting an unusual tetrahedral geometry is prepared and characterized by several spectroscopic methods. The Cu<sup>II</sup>alkylperoxido complex exhibits C–H and O–H bond activation reactivity towards 1,4-cyclohexadiene and phenol derivatives. Mechanistic details are explored by kinetic analysis and DFT calculations, providing important insights into the reactivity of the bioinspired Cu<sup>II</sup>-peroxido complex.



Cu(II)-alkylperoxido in Tetrahedral Geometry Ikuma Shimizu, Yuma Morimoto, Gunasekaran Velmurugan, Tulika Gupta, Sayantan Paria, Takehiro Ohta, Hideki Sugimoto, Takashi Ogura, Peter Comba,\* and Shinobu Itoh\*

Characterization and Reactivity of a Tetrahedral Copper(II)-alkylperoxido Complex

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