

C–H Bond Activation of the Methyl Group of the Supporting Ligand in an Osmium(III) Complex upon Reaction with H₂O₂: Formation of an Organometallic Osmium(IV) Complex

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Supporting Information

ABSTRACT: Oxidation of the hydroxoosmium(III) complex resulted in C–H bond activation of the methyl group of the supporting ligand (*N,N'*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane). The product was an osmium(IV) complex exhibiting a seven-coordinate structure with an additional Os–CH₂ bond.

Metal–oxo species, especially those of the group 8 elements, play key roles in the oxidation processes of organic synthesis^{1–5} as well as in the catalytic cycles of several metalloenzymes in the case of iron.^{6–9} Among the metal–oxo complexes of the group 8 elements, those of ruthenium have been studied most extensively because the synthetic pathway has been well established.^{3–5} Recently, a number of iron–oxo complexes have also been reported, providing important insights into the catalytic mechanism of iron monooxygenases.^{6–9} On the other hand, osmium–oxo complexes have been considered to be less reactive compared with the iron– and ruthenium–oxo complexes because of the low-energy 5d orbitals, stabilizing the oxo complexes by a strong interaction with the p orbitals of the oxygen atom. Thus, little attention has been focused on the reactivity of the osmium–oxo complexes,¹⁰ even though the inorganic osmium(VIII) compounds such as OsO₄^{11,12} and [OsN(O)₃]^{–13,14} have been widely utilized in alkene dihydroxylation and alkane hydroxylation. So far, a number of osmium–oxo complexes with simple (poly)pyridyl ligands were synthesized, but the research target was limited in proton-coupled electron-transfer reactivity generating osmium–hydroxo and osmium–aqua species or photochemical properties.^{15–22}

In this study, we examine the reaction of an osmium(III) complex supported by a macrocyclic tetraaza ligand L (= *N,N'*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane) and H₂O₂ to find aliphatic C–H bond activation, giving an osmium(IV) organometallic complex. The reaction may involve an osmium(V)–oxo species as a key reactive intermediate.

First, dichloro- and dibenzoatoosmium(III) complexes with ligand L, [Os^{III}Cl₂L]PF₆ (**1**) and [Os^{III}(OBz)₂L]PF₆ (**2**), were synthesized as precursors [ChemDraw structures (Chart S1 in the Supporting Information, SI), and synthetic procedures are provided in the SI]. Crystal structures of **1** and **2** are shown in Figure 1, and the crystal graphical parameters are summarized in Tables S1 and S2 in the SI. The Os1 atom of **1** is coordinated with the four nitrogen atoms (N1–N4) from L and the two

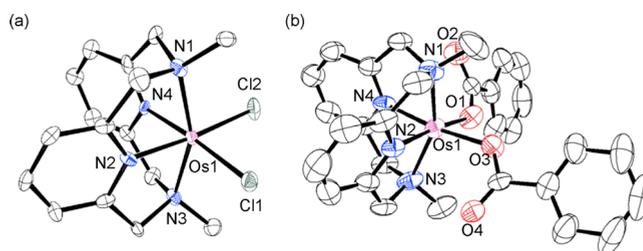


Figure 1. Crystal structures of the cationic parts of **1** (a) and **2** (b) shown in 50% ellipsoids. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1**: Os1–Cl1 2.362(3), Os1–Cl2 2.360(2); Cl1–Os1–N4 175.22(19), Cl2–Os1–N6 173.5(2), N1–Os1–N3 157.1(3). Selected bond lengths (Å) and angles (deg) for **2**: Os1–O1 2.051(4), Os1–O2 2.069(4); O1–Os1–N4 171.57(16), O3–Os1–N2 172.09(14), N1–Os1–N3 154.65(15).

chloride ions (Cl1 and Cl2). The N1–Os1–N3 angle of 157.1(3)° is significantly smaller than the regular angle of 180° in an octahedron, which indicates that the octahedral geometry of the Os1 center is highly distorted. The Os1 atom of **2** also has a highly distorted octahedron, as indicated by the small N1–Os1–N3 angle of 154.65(15)°.

Hydrolysis of **1** and **2** was then examined to obtain osmium(III)–aqua and/or –hydroxo complexes. An aqueous solution of **1** showed an electrospray ionization mass spectrum (ESI-MS) only due to **1**, indicating that the chloride ligands were not replaced by the solvent water molecules. On the other hand, as shown in Figure 2, the ESI-MS spectrum of an aqueous solution of **2** showed a peak cluster at *m/z* 598. The isotopic distribution pattern is consistent with that of [Os^{III}(OH)(OBz)–L]⁺ (**3**), indicating that one of the benzoate ligands of **2** was replaced by a hydroxide ion. Then, the acid–base chemistry of **3** was investigated.²³ Figure S1a in the SI shows the UV–visible spectral change of **3** in the pH titration, where the absorption band at 354 nm due to **3** increases with a contaminant decrease of the absorption bands around 300 nm due to **3H** ([Os^{III}(OH₂)(OBz)L]²⁺, the aqua form of **3**; eq 1) with isosbestic points at 267 and 335 nm as the pH of the solution is raised from 2 to 7. A plot of the absorbance at 354 nm against pH gave a sigmoidal curve (Figure S1a in the SI, inset) ascribable to the acid–base equilibrium between the Os^{III}OH₂ in **3H** and the Os^{III}OH in **3** (eq 1). The p*K*_a value was calculated as 4.5 from the plot of

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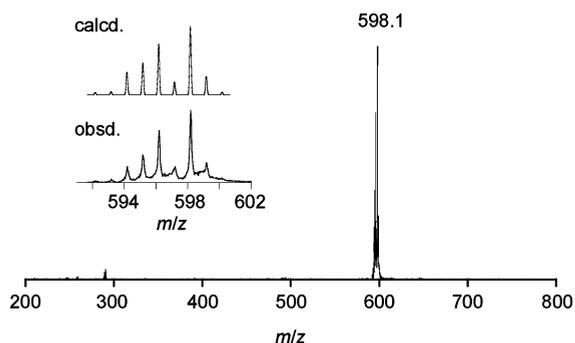
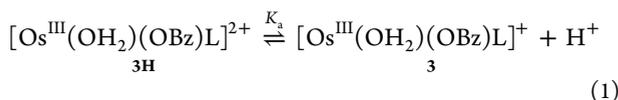


Figure 2. Positive ESI-MS of **3** generated by the treatment of **2** with H_2O . Inset: expanded spectrum around m/z 598 (obsd) and calculated isotopic distribution pattern for **3**.

$\log(A_0 - A)/(A_\infty - A)$ versus the pH (Figure S1b in the SI and eq 1). The value is somewhat larger than that of $[\text{Os}^{\text{III}}(\text{OH}_2)(\text{trpy})(\text{bpy})]^{3+}$ ($\text{p}K_a = 2.0$; $\text{trpy} = 2,2':6',2''$ -terpyridine; $\text{bpy} = 2,2'$ -bipyridine),¹⁵ reflecting the lower Lewis acidity of the osmium(III) center coordinated by the anionic benzoate ligand than that by the noncharged trpy and bpy ligands.



An aqueous solution of **3** was then treated with H_2O_2 under a dinitrogen atmosphere at 70°C .²³ Figure 3a shows the UV–

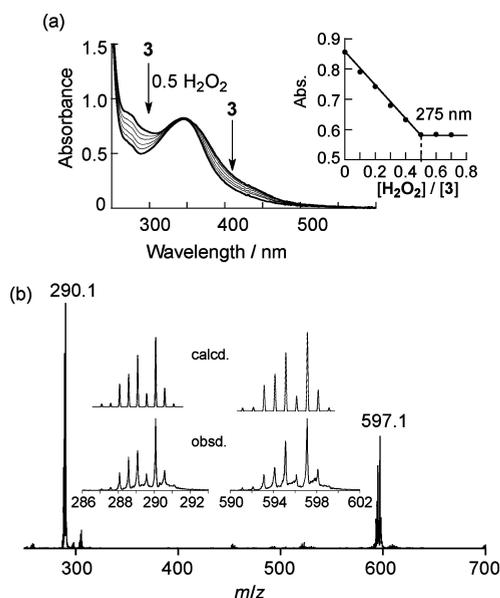


Figure 3. (a) UV–visible spectral changes observed upon addition of $n/10$ equiv of H_2O_2 to **3** ($n = 1-7$; $[\text{3}] = 0.1 \text{ mM}$) in H_2O . Inset: plot of absorbance at 275 nm against the molar ratio of $[\text{H}_2\text{O}_2]/[\text{3}]$. (b) Positive ESI-MS spectrum of a solution measured after the reaction.

visible spectral changes for the titration of **3** with H_2O_2 , where the absorption bands around 280 and 370–470 nm decreased. The plot of absorbance at 275 nm against the molar ratio of $[\text{H}_2\text{O}_2]/[\text{3}]$ (inset) clearly indicates the stoichiometry of $\text{3:H}_2\text{O}_2 = 1:0.5$. As shown in Figure 3b, the ESI-MS spectrum measured after the titration showed two peak clusters at m/z 597.1 as a monocationic pattern and at m/z 290.1 as a dicationic pattern. The isotopic distribution pattern of the parent peak cluster at m/z

597.1 was consistent with that estimated for $[\text{Os}^{\text{IV}}(\text{O})(\text{OBz})\text{L}]^+$ or $[\text{Os}^{\text{IV}}(\text{OH})(\text{OBz})(\text{L}-\text{H})]^+$ ($\text{L}-\text{H}$ denotes a ligand losing one H). Both compounds can be formally generated by one-electron and one-proton loss from **3**. On the other hand, the isotopic distribution pattern of the dicationic peak cluster can be assignable to $[\text{Os}^{\text{IV}}(\text{OBz})_2(\text{L}-\text{H})]^{2+}$. When the dicationic peak cluster is assumed to be a fragment of the parent peak cluster, it may be reasonable to assign the generated complex as $[\text{Os}^{\text{IV}}(\text{OH})(\text{OBz})(\text{L}-\text{H})]^+$ (**4**). Although a single crystal of **4** itself has yet to be obtained, the dibenzoate derivative $[\text{Os}^{\text{IV}}(\text{OBz})_2(\text{L}-\text{H})]^+$ (**5**) was successfully crystallized by concentrating a solution of **4**.

Figure 4 shows the crystal structure of **5**. The Os1 atom is coordinated by the four nitrogen atoms N1, N2, N2*, and N3 of

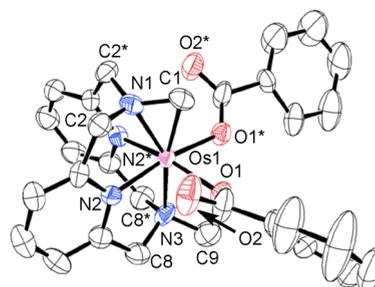


Figure 4. Crystal structure of the cationic part of **5** shown in 50% ellipsoids. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1–O1 2.075(5), Os1–C1 2.101(9); O1–Os1–N2* 167.77(18), N3–Os1–C1 169.9(3), N1–Os1–N3 151.4(3).

$\text{L}-\text{H}$ and the two oxygen atoms O1 and O1* of the two benzoate ligands. Notably, a direct coordination of C1 to Os1 was observed, which made a seven-coordinate osmium center [Os1–C1 bond distance = 2.101(9) Å]. Similar intramolecular bond formation between a metal center and a carbon atom of a tertiary amine macrocyclic ligand was observed in some cobalt(III) complexes, where the Co–C bond length was 1.950(10) Å.^{24,25} The bond angles for O1*–Os1–N2 (=O1–Os1–N2) and N3–Os1–C1 [167.77(18) and 169.9(3)°, respectively] are significantly larger than that of N1–Os1–N3 [151.4(3)°]. Thus, the geometry of the seven-coordinate Os1 atom is best described as a capped octahedron, where N1 acts as the capping ligand. In the ^1H NMR spectrum of **5** in CD_3CN , sharp signals were observed in the range from 3.10 to 7.92 ppm (see the SI), indicating that the spin state of complex **5** is $S = 0$ (singlet). Also, the presence of one PF_6^- counteranion per one complex cation supports the Os^{IV} oxidation state in **5**. Because complex **5** was generated just by a ligand exchange reaction from OH^- in **4** to OBz^- in **5**, it can be concluded that complex **4** has a similar $\text{Os}^{\text{IV}}-\text{CH}_2$ bond.

A possible mechanism for the conversion of **2** to **5** is presented in Scheme S1 in the SI. Because formation of the organometallic $\text{Os}^{\text{IV}}-\text{CH}_2$ bond was not observed in the reaction of the dichloroosmium(III) complex **1** with H_2O_2 in H_2O and **1** hardly underwent hydrolysis, the osmium(III) hydroxo complex **3** formed by hydrolysis of the osmium(III) dibenzoate complex **2** is a starting complex for the C–H bond activation of the methyl group of L. Then, the reaction of **3** and H_2O_2 may provide an osmium(IV) oxo intermediate (**I**) through electron-transfer oxidation followed by deprotonation or via O–O bond homolytic cleavage of a dinuclear osmium- μ -peroxo-type intermediate (not shown in Scheme S1 in the SI). Both reaction pathways are consistent with the observed stoichiometry of

$3:H_2O_2 = 1:0.5$. The possible involvement of intermediate **I** is strongly supported by the fact that the treatment of **3** with 1 equiv of $(NH_4)_2Ce^{IV}(NO_3)_6$ (CAN) or 0.5 equiv of $(NH_4)_2(S_2O_8)$ gave UV–visible and ESI-MS spectra nearly identical with those of **4** produced by the reaction with H_2O_2 . In these cases, one-electron oxidation of **3** gives an osmium(IV) complex, from which deprotonation of the hydroxo ligand takes place to give osmium(IV) oxo intermediate **I**; the pK_a value of the hydroxo ligand of the osmium(IV) complexes supported by pyridine-based ligands was reported to be smaller than 0.^{29,30} From intermediate **I**, C–H bond activation occurs to yield **4** via a radical-type mechanism (hydrogen-atom abstraction concomitant with Os–C bond formation, path A) or an ionic mechanism (proton abstraction and carbanion rebound, path B). It has been reported that C–H bond activation is facilitated by an agnostic interaction in cobalt(III) complexes with a macrocyclic ligand.²⁴ The relatively short distances between Os1 and the methyl carbon atoms as 3.052(7) and 3.069(7) Å in **2** suggest that there is such an agnostic interaction between the osmium center and the methyl group to facilitate Os–C bond formation.^{31,32} Ligand substitution of the OH group in **4** with the benzoate ion gave the crystallographically characterized **5**. It should be noted that the presence of a metal center having both $-CH_2-$ and $-OH$ groups as found in **4** has yet to be reported in other metal complexes because the OH^- ligand attached on a high-valent metal(IV) center inserts into the $M^{IV}-C$ bond to yield a hydroxylated $M^{II}-OCH_2$ -type product.^{1–7}

In summary, the oxidation reactivity of osmium(III) hydroxo complexes was examined to demonstrate that C–H bond activation could proceed to form an organometallic osmium(IV) complex. An osmium(IV) oxo species may be an active species for such a C–H bond activation reaction. The results may provide new insights into the design of metal–oxo complexes for selective oxidations involving C–H bond activation.

■ ASSOCIATED CONTENT

● Supporting Information

X-ray crystallographic data in CIF format, experimental details and characterization data, ChemDraw structures of the complexes (Chart S1), proposed formation mechanism of **4** (Scheme S1), UV–visible spectral changes of **3** and the titration plot (Figure S1), crystallographic data of **1**, **2**, and **5** (Table S1), and selected bond lengths and angles for **1**, **2**, and **5** (Tables S2 and S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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