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C−H Bond Activation of the Methyl Group of the Supporting Ligand in an Osmium(III) Complex upon Reaction with H_2O_2: 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−CH_2 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 OsO_4[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 H_2O_2 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, $[Os^{III}Cl_2L]PF_6$ (**1**) and $[Os^{III}(OBz)_2L]PF_6$ (**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 chloride ions (Cl1 and Cl2). The N1−Os1−N3 angle of 157.1(3)° is significantly smaller than the regular angle of 180° in a 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)°.

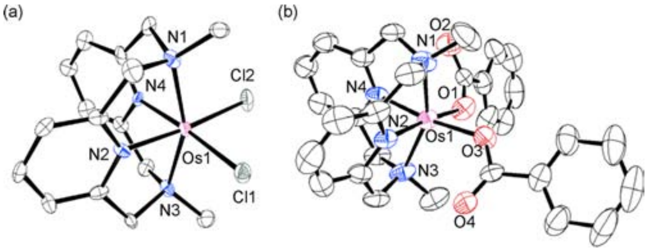

Figure 1. Crystal structures of the cationic parts of **1** (a) and **2** (b) shown in 50% ellipsoids. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1**: Os1−Cl1 2.362(3), Os1−Cl2 2.360(2); Cl1−Os1−N4 175.22(19), Cl2−Os1−N6 173.5(2), N1−Os1−N3 157.1(3). 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).

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** ($[Os^{III}(OH_2)(OBz)L]^{2+}$, 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 $Os^{III}OH_2$ in **3H** and the $Os^{III}OH$ in **3** (eq 1). The pK_a value was calculated as 4.5 from the plot of

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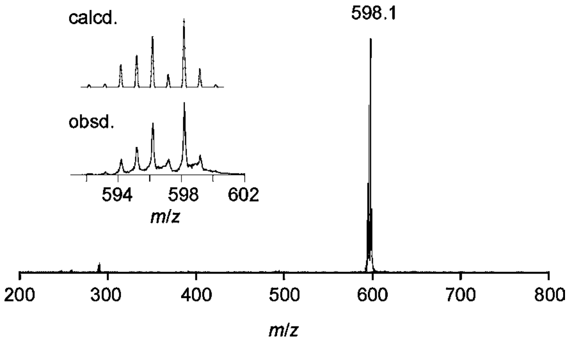

Figure 2. Positive ESI-MS of **3** generated by the treatment of **2** with H_2O. Inset: expanded spectrum around m/z 598 (obsd) and calculated isotopic distribution pattern for **3**.

$\log(A_0 - A)/(A_\infty - A)$ versus the pH (Figure S1b in the SI and eq 1). The value is somewhat larger than that of $[Os^{III}(OH_2)(trpy)(bpy)]^{3+}$ (pK_a = 2.0; trpy = 2,2′:6′,2″-terpyridine; 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.

$$\underset{\mathbf{3H}}{[Os^{III}(OH_2)(OBz)L]^{2+}} \overset{K_a}{\rightleftharpoons} \underset{\mathbf{3}}{[Os^{III}(OH_2)(OBz)L]^{+}} + H^+ \qquad (1)$$

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−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 $[H_2O_2]/[\mathbf{3}]$ (inset) clearly indicates the stoichiometry of $\mathbf{3}:H_2O_2$ = 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 $[Os^{IV}(O)(OBz)L]^+$ or $[Os^{IV}(OH)(OBz)(L{-}H)]^+$ (L−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 $[Os^{IV}(OBz)(L{-}H)]^{2+}$. 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 $[Os^{IV}(OH)(OBz)(L{-}H)]^+$ (**4**). Although a single crystal of **4** itself has yet to be obtained, the dibenzoate derivative $[Os^{IV}(OBz)_2(L{-}H)]^+$ (**5**) was successfully crystallized by concentrating a solution of **4**.

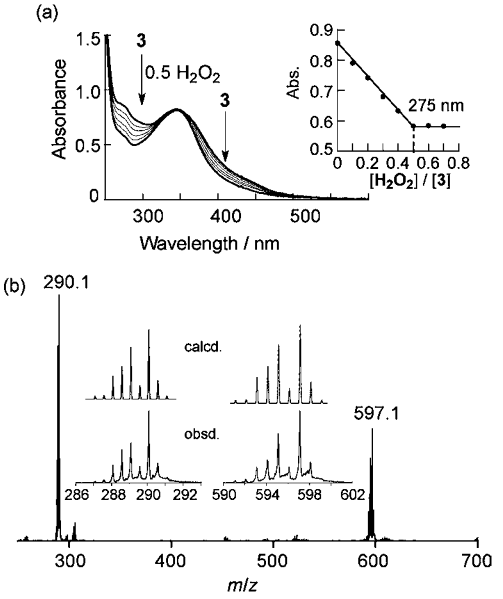

Figure 3. (a) UV−visible spectral changes observed upon addition of n/10 equiv of H_2O_2 to **3** (n = 1−7; [**3**] = 0.1 mM) in H_2O. Inset: plot of absorbance at 275 nm against the molar ratio of $[H_2O_2]/[\mathbf{3}]$. (b) Positive ESI-MS spectrum of a solution measured after the reaction.

Figure 4 shows the crystal structure of **5**. The Os1 atom is coordinated by the four nitrogen atoms N1, N2, N2*, and N3 of L−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 $Os^{IV}{-}CH_2$ bond.

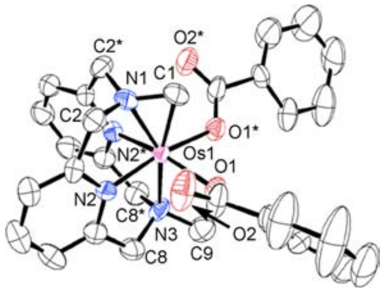

Figure 4. Crystal structure of the cationic part of **5** shown in 50% ellipsoids. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1−O1 2.075(5), Os1−C1 2.101(9); O1−Os1−N2* 167.77(18), N3−Os1−C1 169.9(3), N1−Os1−N3 151.4(3).

A possible mechanism for the conversion of **2** to **5** is presented in Scheme S1 in the SI. Because formation of the organometallic $Os^{IV}{-}CH_2$ 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 organomatallic 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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