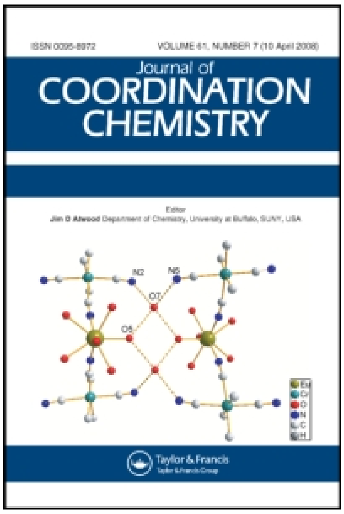

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Unexpected μ-oxo five-member ring intermediates for oxygen atom transfer between osmium complexes

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Unexpected μ-oxo five-member ring intermediates for oxygen atom transfer between osmium complexes

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The reaction mechanisms for oxygen atom transfer between $O=OsL_3$ and OsL_3 with ligands of different sizes (L = NMe, NPh, Nmes, NAr) were studied by using density functional theory. In contrast to a previously proposed transition state with a linear Os–O–Os structure, an unexpected μ-oxo five-member diosmium ring with an N–N bonded structure is discovered as an intermediate for the transfer of oxygen. An isomeric five-member ring structure with an N–O bond is also found. Computational results indicate that the steric effects of bulky ligands play an important role in the geometry of dimetal complexes, and strongly affect the reaction kinetics.

Keywords: Oxygen atom transfer; Osmium; Reaction mechanism; μ-Oxo dimetal ring

1. Introduction

Oxygen-atom-transfer (OAT) reactions catalyzed by transition metal complexes play important roles in oxidations [1], in carbon−hydrogen bond activations [2], and in metalloenzymes such as sulfite oxidase and DMSO reductase, where Mo or W act as the catalytic centers [3]. Unlike the understanding of single-electron transfer rate provided by Marcus theory, the factors that affect the rates of OAT is still not clear. Brown and coworkers [4] recently reported a study of OAT between two late metal centers. They found that the oxygen transfer rate between $(mes)_3Ir=O$ (mes = 2,4,6-trimethylphenyl) and its deoxy partner $(mes)_3Ir$ is 12 orders of magnitude faster than the transfer rate between $(NAr)_3Os=O$ (Ar = 2,6-diisopropylphenyl), and $(NAr)_3Os$, while the rate of OAT between $(mes)_3Ir=O$ and $Os(NAr)_3$ is intermediate, the first observation of the Marcus cross-relation in OAT reactions. In their density functional theory (DFT) study of model complexes with Me and NMe ligands, they found an intermediate and a transition state with a low barrier for the oxygen transfer in the diiridium system. This is confirmed by the observation of a μ-oxo bridged intermediate for the Ir system at low temperature. However, they were unable to find a stable intermediate or a transition state for μ-oxo complex $(MeN)_3Os–O–Os(NMe)_3$ in their calculation. The role of steric effect of bulky ligands in these reactions was not investigated nor is it well understood. Recently, Sakaki and coworkers [5] investigated theoretically the effect of bulky ligands

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on the structure of these dinuclear Ir and Os complexes using DFT methods and obtained a transition state with linear Os–O–Os structure for OAT between $OOs(NAr)_3$, and $Os(NAr)_3$ with an activation free energy of $52.6\,\mathrm{kcal\,mol^{-1}}$ in the gas-phase.

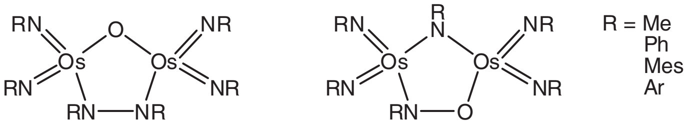
As described below, in addition to the linear Os–O–Os transition state for the direct transfer of oxygen between two Os complexes, our application of DFT discovered an unexpected, stable five-membered μ-oxo diosmium ring structure as an intermediate for the transfer of oxygen between two Os complexes. Another five-member diosmium ring structure, which is an isomer of the μ-oxo complex with an N–O bond, is also found in our calculations. The steric effect of different ligands is analyzed based on the calculated relative energies of intermediates and transition states.

2. Computational details

All calculations were performed using the Gaussian 03 suite of *ab initio* programs [6] at the Tao–Perdew–Staroverov–Scuseria (TPSS) [7] functional with Pople type all-electron 6-31G(d′) basis set [8] for H, C, N, and O atoms and Stuttgart quasi-relativistic effect core potential basis set (ECP60MWB) for Os [9] (1428 basis functions and 2820 primitive Gaussians for the NAr ligand). We believe such basis sets are sufficient for accurate DFT calculations [10]. The geometric structures of all species were optimized as gas-phase. Calculating the harmonic vibrational frequencies and noting the number of imaginary frequencies (IF) confirmed the nature of all intermediates (no IF) and transition state structures (only one IF). The latter were also confirmed to connect reactants and products by intrinsic reaction coordinate (IRC) calculations. The gas-phase enthalpy (H), and free energies (G), were calculated at $T = 298.15\,\mathrm{K}$ within the harmonic potential approximation at optimized structures. The 3-D molecular structures displayed in this article were drawn using the JIMP2 molecular visualizing and manipulating program [11].

3. Results and discussion

Four different sets of ligands were examined for the oxygen exchange between $OOsL_3$ and its deoxy partner OsL_3 (L = NMe, NPh, Nmes (mes = 2,4,6-trimethylphenyl) and NAr (Ar = 2,6-diisopropylphenyl)) (scheme 1). Two types of stable five-member diosmium ring structures with similar relative energies are discovered. Among these ring structures, the μ-oxo diosmium complexes with an N–N bond in the ring (**1-R**) can act as intermediates for OAT between $OOsL_3$ and OsL_3. We were unable to find a linear Os–O–Os transitions state for direct oxygen transfer between two Os complexes using the current computational method and any of the ligand sets. However, using smaller Stuttgart ECP basis for all atoms, we can locate a linear Os–O–Os transition state for direct oxygen transfer between $OOs(NAr)_3$ and $Os(NAr)_3$ with a energy barrier close to the previous theoretical study [5]. Here, we do not repeat those reported results, but focus on the newly predicted ring structures for possible low-barrier OAT reaction pathways.



1-R **2-R**

Scheme 1. Five-member ring structures of OOs_2L_6.

3.1. *Five-member μ-oxo diosmium ring structures*

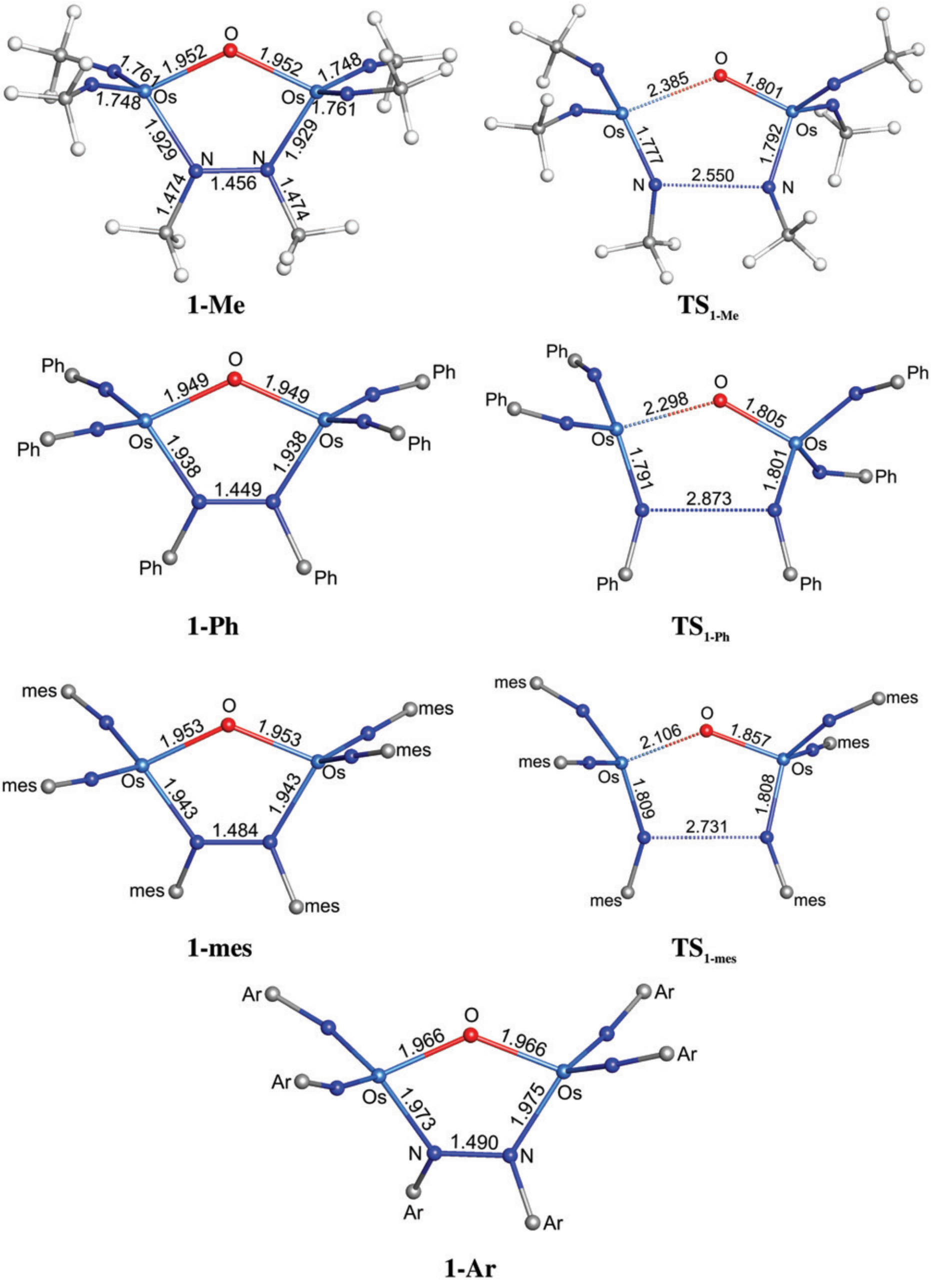
The optimized five-member μ-oxo ring structures of OOs_2L_6 and the corresponding transition states for their formation and dissociation are shown in figure 1. These μ-oxo ring structures are formed through direct combination of $OOsL_3$ and OsL_3 with the simultaneous formation of an Os–O bond and a N–N bond in each structure. The oxygen atom can be transferred between two osmium centers through the formation and breaking of the symmetric Os–O bonds. Their relative energies are shown in table 1. The gas-phase free energy profile for these reactions is shown in figure 2.

For the NMe ligand, the transition state $\mathbf{TS_{1\text{-}Me}}$ is 10.1 kcal mol^{-1} higher than reactants $OOs(NMe)_3$ and $Os(NMe)_3$ in gas-phase enthalpy. The five-member diosmium μ-oxo ring intermediate **1-Me** is 10.7 kcal mol^{-1}, more stable than separated Os complexes. The N–N distance in **1-Me** is 1.456 Å, indicating a strong N–N single bond. Although **1-Me** could be easily formed, its dissociation would be slow because of an enthalpic barrier of more than 20 kcal mol^{-1}. Therefore, the OAT is predicted to be slow between $OOs(NMe)_3$ and $Os(NMe)_3$ because the oxygen atom is "trapped" in **1-Me**.

For the NPh ligand, the N–N and O–Os bond lengths in **1-Ph** are slightly shorter than those in **1-Me**, while the N–Os bonds in the ring are slightly (0.01 Å) longer. Although the enthalpy of the **1-Ph** intermediate is much higher than the relative energies of **1-Me**, the transition state ($\mathbf{TS_{1\text{-}Ph}}$) for formation of **1-Ph** is about 1 kcal mol^{-1} lower than that for $\mathbf{TS_{1\text{-}Me}}$. These results predict that the oxygen atom can be transferred between $OOs(NPh)_3$ and $Os(NPh)_3$ through the formation and dissociation of **1-Ph**.

For the Nmes ligand, due to the stronger steric effect caused by the bulky structure of mes, all bonds in the μ-oxo ring of **1-mes** are slightly longer than those in **1-Me** and **1-Ph**. The relative enthalpy and free energy of $\mathbf{TS_{1\text{-}mes}}$ are 14.3 and 31.6 kcal mol^{-1}, much higher than those of $\mathbf{TS_{1\text{-}Me}}$ and $\mathbf{TS_{1\text{-}Ph}}$. The barely stable structure in **1-mes** is 10.3 and 30.6 kcal mol^{-1} higher in enthalpy and free energy relative to reactants. These results predict that the OAT between $OOs(Nmes)_3$ and $Os(Nmes)_3$ is slow because of the high energy barrier for the formation of **1-mes**.

For the NAr ligand, although we obtained the five-member μ-oxo ring structure, we were unable to locate a transition state similar to that found with other ligands for the formation of μ-oxo ring. We believe this is due to the very strong steric effect of the Ar ligands, which makes the transition state $\mathbf{TS_{1\text{-}Ar}}$ and the intermediate **1-Ar** very close in relative energies, and both of them are much higher than the relative energies of the μ-oxo complexes with other smaller ligands. The O–Os, N–Os, and N–N bonds in the five-member ring of **1-Ar** are all longer than those bonds in the μ-oxo ring formed with other ligands, an illustration of the steric effect of bulky NAr ligands.



1-Me $TS_{1\text{-}Me}$

1-Ph $TS_{1\text{-}Ph}$

1-mes $TS_{1\text{-}mes}$

1-Ar

Figure 1. Optimized μ-oxo ring structures of OOs_2L_6 (L = NMe, NPh, Nmes, and NAr) and the corresponding transition states for their formation and dissociation. The bond lengths are in angstroms.

3.2. *Five-member ring isomers*

In addition to the above μ-oxo structures, five-member ring isomers with an N–O bond and a new Os–N bond were also found in our calculations. The optimized structures of **2-Me**, **2-Ph**, **2-mes**, and **2-Ar** and the corresponding transition states for their formation

Table 1. Gas-phase relative electronic energies (ΔE), enthalpies (ΔH), and free energies (ΔG) of the structures shown in figure 1 (kcal mol^{-1}).

	ΔE	ΔH	ΔG
$Os(NMe)_3 + OOs(NMe)_3$	0.0	0.0	0.0
$\mathbf{TS_{1\text{-}Me}}$	10.1	10.1	23.4
1-Me	−12.6	−10.7	5.4
$Os(NPh)_3 + OOs(NPh)_3$	0.0	0.0	0.0
$\mathbf{TS_{1\text{-}Ph}}$	8.9	8.7	22.4
1-Ph	1.0	0.2	15.1
$Os(Nmes)_3 + OOs(Nmes)_3$	0.0	0.0	0.0
$\mathbf{TS_{1\text{-}mes}}$	14.6	14.3	31.6
1-mes	9.0	10.3	30.5
$Os(NAr)_3 + OOs(NAr)_3$	0.0	0.0	0.0
$\mathbf{TS_{1\text{-}Ar}}$	–	–	–
1-Ar	30.7	32.4	48.4

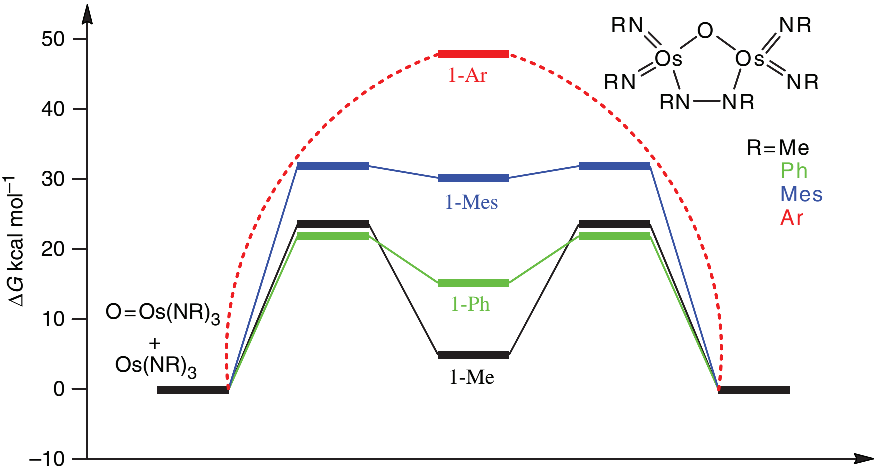
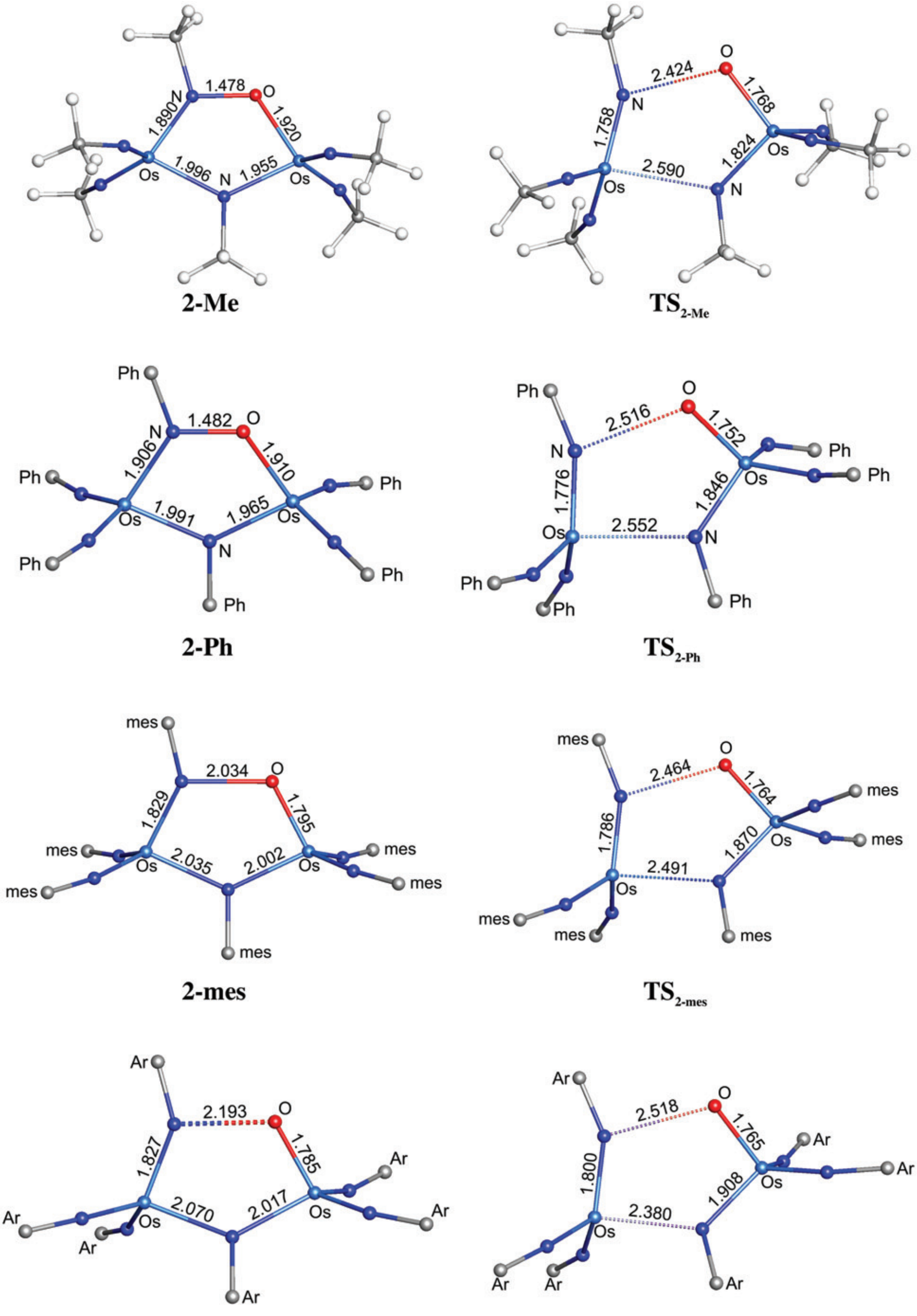


Figure 2. Gas-phase free energy profile for the formation and dissociation of μ-oxo ring structures OOs_2L_6 (L = NMe, NPh, Nmes, and NAr).

and dissociation are shown in figure 3. Their relative energies are shown in table 2. These ring structures are formed through direct combination of $OOsL_3$ and OsL_3 with simultaneous formation of an Os–N bond and an N–O bond in each structure. Since these five-member species lack the μ-oxo diosomium bond, they cannot transfer an oxygen atom between two osmium complexes.

For the NMe ligand, the stable ring structure **2-Me** is 6.5 kcal mol^{-1} lower and 8.6 kcal mol^{-1} higher than reactants $OOs(NMe)_3$ and $Os(NMe)_3$ in gas-phase enthalpy and free energy. The corresponding transition states $\mathbf{TS_{2\text{-}Me}}$ are 7.5 and 20.6 kcal mol^{-1} higher than the reactants. Such low energy barrier predicts fast formation and dissociation of **2-Me**. The N–O distance in **2-Me** is 1.478 Å, indicating a strong N–O single bond. Although **2-Me** is less stable than **1-Me**, the barrier to its formation is lower.

For the NPh ligand, the N–O bond in **2-Ph** is only slightly longer than that in **2-Me**. Like **1-Ph**, the enthalpy of **2-Ph** is very close to that of the reactants, but the transition



2-Me **TS$_{2\text{-Me}}$**

2-Ph **TS$_{2\text{-Ph}}$**

2-mes **TS$_{2\text{-mes}}$**

2-Ar **TS$_{2\text{-Ar}}$**

Figure 3. Optimized stable five-member ring diosmium isomers and the corresponding transition states for their formation and dissociation. The bond lengths are in angstroms.

Table 2. Gas-phase relative electronic energies (ΔE), enthalpies (ΔH), and free energies (ΔG) of the structures shown in figure 3 (kcal mol^{-1}).

	ΔE	ΔH	ΔG
$Os(NMe)_3 + OOs(NMe)_3$	0.0	0.0	0.0
TS$_{\textbf{2-Me}}$	7.2	7.5	20.6
2-Me	−7.9	−6.5	8.6
$Os(NPh)_3 + OOs(NPh)_3$	0.0	0.0	0.0
TS$_{\textbf{2-Ph}}$	11.0	11.0	24.0
2-Ph	1.1	2.0	14.7
$Os(Nmes)_3 + OOs(Nmes)_3$	0.0	0.0	0.0
TS$_{\textbf{2-mes}}$	14.3	13.8	32.7
2-mes	9.4	9.8	27.9
$Os(NAr)_3 + OOs(NAr)_3$	0.0	0.0	0.0
TS$_{\textbf{2-Ar}}$	–	–	–
2-Ar	29.7	30.9	45.2

state **TS$_{\textbf{2-Ph}}$** for the formation of **2-Ph** is about 2 kcal mol^{-1} higher than **TS$_{\textbf{1-Ph}}$**. The relative free energies of **TS$_{\textbf{2-Ph}}$** and **2-Ph** are 24.0 and 14.7 kcal mol^{-1}, respectively, predicting slower formation and faster dissociation of **2-Ph**.

Because of the strong steric effect of Nmes, the N–O distance in **2-mes** is much longer than in **2-Me** and **2-Ph**. The stable structure of **2-mes** is 9.8 and 27.9 kcal mol^{-1} higher than the reactants $OOs(Nmes)_3$ and $Os(Nmes)_3$ in enthalpy and free energy, respectively. The corresponding transition state **TS$_{\textbf{2-mes}}$** has relative enthalpy and free energy of 13.8 and 32.7 kcal mol^{-1}, indicating that **2-mes** is difficult to form but easy to dissociate.

Like **1-Ar**, the very strong steric effect of the NAr ligands leads **2-Ar** to be 30.9 and 45.2 kcal mol^{-1} higher than the reactants in enthalpy and free energy. However, the relative enthalpy and free energy of **2-Ar** are about 2 kcal mol^{-1} lower than those of **1-Ar**, in part because the short N–N bond in **1-Ar** brings the bulky NAr ligands close. These results indicate that **2-Ar** is also difficult to form and would not be observed experimentally because of its short lifetime.

4. Conclusion

Unexpected, relatively stable five-member μ-oxo rings with strong N–N single bond intermediates and their isomers with a N–O bond in the five-member ring were predicted in the DFT study of oxygen atom transfer between $O=OsL_3$ and OsL_3 ($L = NMe$, NPh, Nmes, and NAr). There is a somewhat distant precedent for the formation of five-member μ-oxo IrOs ring by the addition of OsO_4 to the Ir–C bond reported by Collins and coworkers [12] more than two decades ago. The steric effect of bulky ligands plays important roles in both the geometric structure of dimetal complexes and the reaction kinetics. The ultraslow oxygen atom transfer between $O=Os(NAr)_3$ and $Os(NAr)_3$ [4] is a result of the bulky Ar ligands, which lead to very high energy barriers for both the formation of μ-oxo diosmium complex $OOs_2N_6Ar_6$ or the direct transfer of oxygen atom through linear Os–O–Os transition state predicted by Sakaki and coworkers [5]. The simultaneous formation of N–N and O–Os bonds in the μ-oxo complexes and the formation of N–O and N–Os bonds in their isomers stabilize the electron acceptor orbitals of $O{=}OsL_3$ in the ring structures. A new oxygen atom transfer mechanism is predicted through the stability of these intermediates. The reductive elimination of the Os–N π bonds and the formation of the N–N (or N–O) bonds provide a more stable μ-oxo dimer intermediate by reducing the high electron count on the Os centers that could have existed in the linear Os–O–Os transition state.

Supplementary material

Atomic coordinates of optimized stationary points and transition states.

Acknowledgments

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