

Regioselective Knitting of Aniline *via ortho*-C–N Bond Fusion Using OsO₄ as a Template

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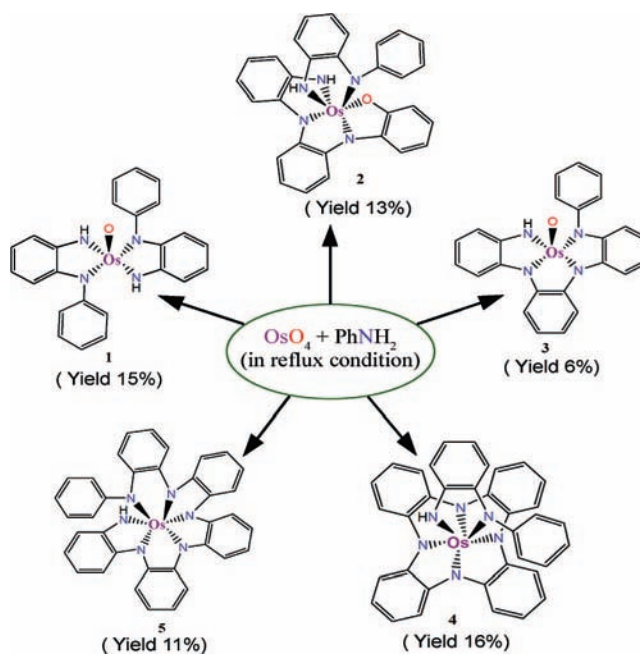
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Synthesis of complicated molecules by using a simpler route is one of the important challenges to synthetic chemists. Transition metal mediated carbon–heteroatom bond formation reactions^{1–4} *via* C–H activation is a vital tool for achieving this goal. In this communication we disclose the first examples of OsO₄ mediated regioselective knitting of aniline moieties *via ortho*-C_{arom}–N fusion. Oxidation chemistry of anilines is varied,⁵ and its oxidative fusion reactions commonly give hydrazine, azo, or azoxy compounds. Because of its high electron-rich aromatic behavior, use of aniline^{6,7} as a coupling partner for C–N fusion reaction is rather unusual. However, metal mediated and/or electrochemical oxidative oligomerization of aniline to polyanilines *via para*-C–N coupling has been long known.⁸ In comparison, similar multiple *ortho*-C–N fusion of aniline is not available in the literature.

We have a long standing interest^{9,10} in the metal promoted oxidative *ortho*-C–N fusion reactions of aniline. Thus far nonoxo Ru(III) and Os(IV) complexes have been used as the mediators. These reactions occurred only in neat condition and led to the dimerization of aromatic amines. However, in a recent publication⁹ we have shown that a similar *ortho*-C–N bond fusion can be achieved in solution as well by the highly oxidizing osmium tetroxide. The reaction unexpectedly produced a mono-oxo osmium(VI) complex (**1**) of the *N*-phenyl-1,2-diamide ligand. An unusual reaction affinity¹¹ of OsO₄ toward the formation of high valent metal imides drives this reaction cleanly even in solution. This result has encouraged us to extend the reaction further in neat aniline, where a higher number of aniline coordination and subsequent multiple *ortho*-C–N fusion were anticipated.

Four new osmium complexes (**2–5**) of multidentate nitrogen donors are isolated along with⁹ the compound **1** (Scheme 1) from the reaction of OsO₄ with aniline (in neat). The most remarkable part of this chemical reaction is the fusion of aniline producing its higher homologues: di-(**1**), tri-(**2**), tetra-(**3,4**), and hexamer (**5**) *via ortho*-C–N bond construction. Notably, the trianilido ligand in the complex **3** has undergone an additional *ortho*-hydroxylation forming a tetradentate N₃O donor. The aniline tetramer in the complex **4**, on the other hand, has undergone a ring closure reaction with a new C–N bond formation producing a novel N₄-macrocycle. Notably, each of the complexes **2** and **4** also contains *N*-phenyl-1,2-diamide as a coligand. The complex **5** is a unique example of osmium hexamide. For further elucidation of the above transformations, a similar reaction of OsO₄ with *N*-phenyl-1,2-diamino benzene (semidine) has also been studied. The later reaction yielded the nonoxo complexes **4** and **5** along with a strongly fluorescent compound whose identity is yet to be established. It may be noted here that a similar reaction⁹ of semidine in heptane produces the mono-oxo complex **1** in a high yield.

Scheme 1



In a typical reaction OsO₄ was heated at reflux in aniline (10 mL) in the presence of air for 60 h. The crude mass, thus obtained, was purified on a silica gel TLC plate eluting with toluene–hexane solvent mixture (1:4). Microanalytical, positive-ion ESI-mass spectra, together with the NMR spectral data of the compounds **1–5** convincingly support their formulations as shown in Scheme 1. Characterization data of the compounds are submitted as Supporting Information (Figures S1–S4). The identities of the complexes were confirmed by the determination of their X-ray structures. Molecular views of the four new compounds **2–5** are displayed in Figures 1 and 2, and their ORTEP are submitted¹² as Supporting Information (Figures S5–S8).

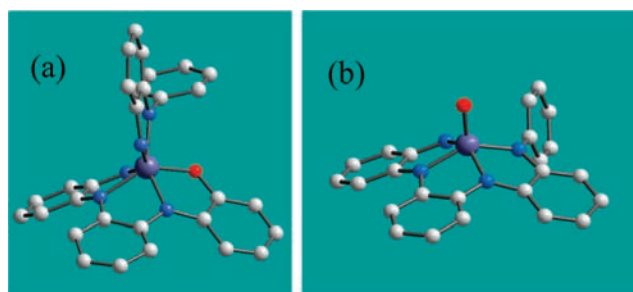


Figure 1. Molecular views of (a) **2** and (b) **3**.

Bond parameters (Supporting Information Table S1) of these complexes indicate that the ligands are coordinated to hexavalent osmium center in their reduced amido state.

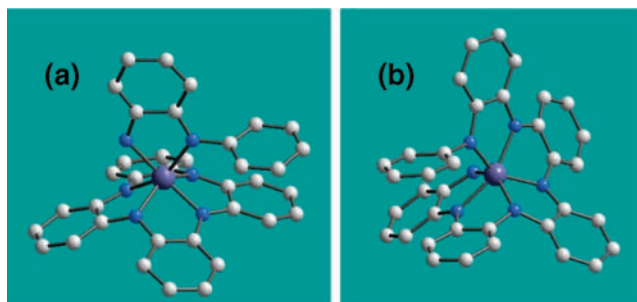


Figure 2. Molecular views of (a) **4** and (b) **5**.

The analyses of X-ray crystal structures of the complexes **2–5** reveal that the osmium metal lies in a highly distorted coordination environment. The complex **3** is a distorted square pyramid with $\tau = 0.06$, whereas the geometry of the hexa coordinated complexes **2**, **4** and **5** are close to trigonal prism with a small trigonal twist angle (Θ) 13.9°, 22.8°, and, 18.0°, respectively.

The mechanism of the reaction remains unresolved as yet. However, it is believed that the formation of an imido intermediate is the key step^{2,6} for activation of *ortho*-C–H bond of the coordinated anilido ligands. The strong oxidizing character of OsO₄ propagates multiple C–N bond fusion in this reaction. Under neat conditions, the local concentration of aniline is highly likely to result in the facile coordination of the multiple anilido substrates to osmium. Since osmium could accommodate (common coordination number, 6) a maximum of six anilido substrates, the reaction has produced a complex of the hexanilido ligand along with the complexes of its lower homologues. Our result thus reconfirms^{10c} that *cis* coordination of aromatic amine substrates is an essential prerequisite for *ortho*-C–N fusion. Furthermore, formation of the complexes from the above reaction involves multiple electron oxidation processes. In comparison, the oxidation state of osmium in the products is only two units less than that in the starting OsO₄. So some other oxidizing agent must have participated in the reaction to compensate the additional electron transfer for the oxidation of aniline. Considering the fact that the above reaction does not occur similarly⁹ in an inert atmosphere, we presume that aerial oxygen participates in the above chemical transformation. Our experiments however have not excluded the possibility of involvement of OsO₄ as one of the oxidants.

Cyclic voltammetric studies on the osmium complexes show multiple electron transfer responses. Generally the reduction waves appeared in the range –0.9 to –1.6 V and are reversible. The two successive oxidative waves in the complexes **2**, **4**, and **5** are reversible, while that for the complex **3** is irreversible. The EPR spectrum of each of the electrogenerated complexes [2]⁺, [4]⁺, and [5]⁺ shows a characteristic sharp (near $g = 2.000$) signal signifying ligand oxidation. Notably oxidation of the reference amido ligands in the above complexes would produce either aminyl or semi-quinone radicals.¹³ Our efforts to isolate and characterize the oxidized complexes are in progress.

In summary, we have disclosed here the first examples of multiple *ortho*-C_{arom}–N bond formation in an anilido substrate. The

chemical reaction has produced the higher homologues of aniline *via* *ortho*-C–N bond fusion. A ring closure reaction in the aniline tetramer produced an unprecedented N₄-macrocyclic. Syntheses of such polyanilido chelates are otherwise not achievable. As a part of our blueprint for *ortho*-C–N bond construction in aromatic amines, we have used strongly oxidizing osmium tetroxide as the template. This work may also be viewed as the beginning of a novel approach to the synthesis of polyamido ligands and their metal complexes. Redox chemistry of such complexes containing redox noninnocent ligands is rich and has been the focus of many important studies in recent times because of their biological relevance.

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Supporting Information Available: X-ray crystallographic files in CIF format for **2–5**; ESI-MS spectra (S1–S4), ORTEP and atom numbering scheme of **2–5** (S5–S8) are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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