Tuning of the o-C$_{arom}$—N Bond-Formation Reactivity of Aniline Using Ruthenium(II) Templates

Subhas Samanta and Sreebrata Goswami*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India

S *Supporting Information*

ABSTRACT: Chemical reactions of aniline with two face-capped ruthenium(II) templates viz. CpRu^{II}Cl(PPh$_3$)$_2$ and (Bnz)$_2$Ru$^{II}_2$Cl$_4$ have been studied to develop an insight into the role of the metal template for the rare type of o-C$_{arom}$—N bond-forming reaction in aniline.

Carbon—nitrogen bond formation in aniline[1−3] is one of the most important reactions for the syntheses of nitrogen-containing aromatic organic compounds that are ubiquitous in modern society as medicines and functional materials.[4] Polyaniline is one of such prominent examples that are of paramount importance[5] as conducting polymers. These are commonly synthesized[6] by the electrochemical or chemical oxidation reaction (Scheme 1), which occurs via successive p-C$_{arom}$—N coupling reactions. In contrast, the corresponding o-C$_{arom}$—N bond-fusion reaction has scarcely been observed. Acid-catalyzed rearrangement of hydrazobenzene to semidine is the only textbook example[7] for the synthesis of the ortho dimer of aniline. Recently, we have discovered[8] that strongly oxidizing OsO$_4$ can be used as a template for bringing about multiple o-C$_{arom}$—N bond-forming reactions in aniline (Scheme 1). In this report, we describe an investigation that has led to the development of an insight into the controlling factors that are responsible for the o-C$_{arom}$—N bond-fusion reactions.

Scheme 1. C$_{arom}$—N Bond-Fusion Reactions in Aniline
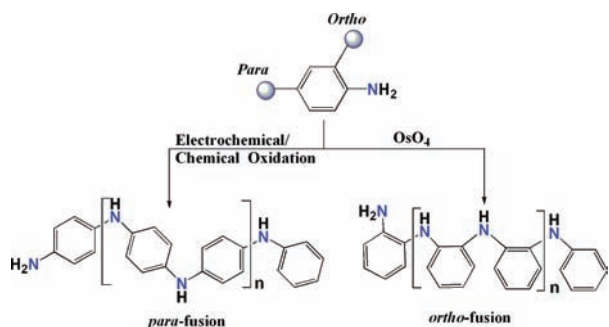
We have been working[8,9] on metal-promoted regioselective ortho dimerization of aniline via C$_{arom}$—N bond-fusion reaction for quite some time. The first example of such a reaction was reported by us nearly a decade ago.[9a] Our results so far have established that the high-valent metal-mediator complexes having labile coordination sites are crucial for bringing about[9a−c] the above reactions. Similar arguments in favor of using high-valent metal-mediator complexes for C$_{arom}$—N bond fusion in electron-rich anilido substrates were put forward by others.[10] It has now been shown that the lability of the mediator complexes is a prerequisite for providing cis-geometrical coordination of aniline for o-C$_{arom}$—N bond fusion.[9] However, the lability in a high-valent metal-mediator complex is usually poor, which causes difficulty in finding a suitable metal-mediator complex for o-C$_{arom}$—N bond-forming reactions.
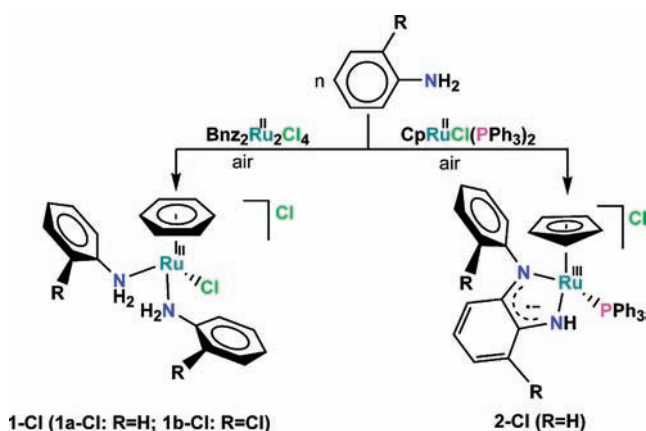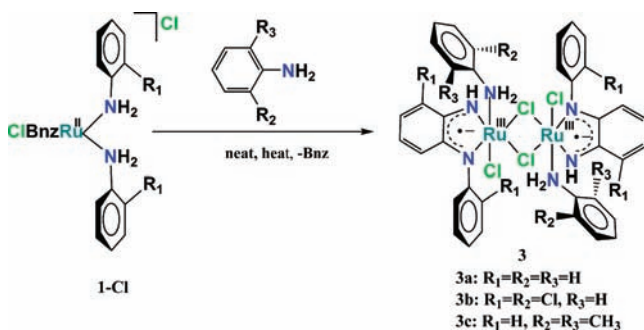
Herein we disclose some novel results of a few planned chemical reactions to demonstrate that the use of oxidizable low-valent metal-mediator complexes can be a viable solution to the above problem. We began our studies with the reactions of anilines using the two ruthenium(II)-mediator complexes, viz., (Bnz)$_2$Ru$^{II}_2$Cl$_4$ (Bnz = benzene) and CpRu^{II}Cl(PPh$_3$)$_2$ (Cp$^-$ = cyclopentadienyl anion). Our primary purpose for selecting these complexes originated from the consideration that these face-capped complexes can offer only cis geometry to the incoming aniline ligands. The redox behaviors of the two chosen mediators are, however, different. While the benzene complex is redox-inert, its analogous Ru^{II}Cp complex is susceptible to oxidation.[11] It is worth noting here that Bnz as a coligand in a complex strongly resists[12] oxidation of the metal center because of its superior π-accepting ability.

In line with our strategy, a suspension of (Bnz)$_2$Ru$^{II}_2$Cl$_4$ in aniline was stirred at 40−50 °C in air. A *cis*-bisaniline complex (**1-Cl**) was isolated from the reaction mixture in high yield, 85%. In contrast, a similar chemical reaction of aniline and CpRu^{II}Cl-(PPh$_3$)$_2$ produced a new complex of the *N*-phenyl-1,2-diaminobenzene ligand (**2-Cl**), formed because of the dimerization of aniline via o-C$_{arom}$—N bond fusion. The two reference reactions are depicted in Scheme 2 for comparison. These results thus indicate that the oxidizable Ru^{II}Cp complex allows oxidative o-C$_{arom}$—N bond fusion, while its redox-inert congener fails to bring about such a bond-fusion reaction in spite of cis coordination of two aniline ligands. However, the complex **1-Cl**, when heated at 373 K in the presence of aniline or 2-chloroaniline produced a new diruthenium complex, **3**, in moderate yield, 35% (Scheme 3). The most notable observations in this conversion, **1-Cl → 3**, is that o-C$_{arom}$—N bond-forming reactions occurred only when the Bnz ligand is substituted by an aromatic amine. This is as anticipated because the intermediate complex lost its redox-inert character because of the loss of the Bnz ligand.[12] We note here that the complex **1-Cl** remained unreactive in boiling

Scheme 2. Reactions of Aniline with Two Mediator Complexes

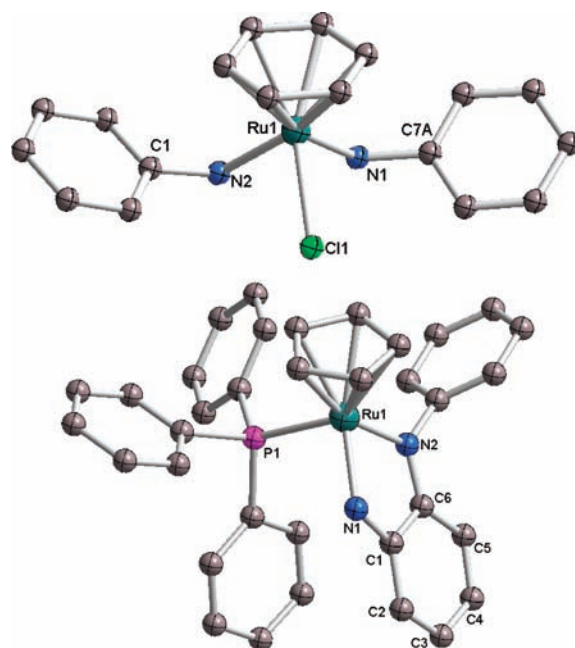**Scheme 3.** *o*-C$_{aorm}$—N Bond Fusion in an Oxidizable Condition

Figure 1. Molecular views of the complexes **1-Cl** (top) and **2-Cl** (bottom). Counteranions and hydrogen atoms are omitted for clarity. Selected bond lengths for **1-Cl**: Ru1—N1, 2.153(2); Ru1—N2, 2.162(2). Selected bond lengths for **2-Cl**: Ru1—N1, 1.992(4); Ru1—N2, 2.024(4); C1—N1, 1.331(6); C2—C1, 1.425(8); C3—C2, 1.353(8); C4—C3, 1.436(8); C5—C4, 1.362(9); C6—C5, 1.429(7); C6—N2, 1.336(6).

toluene (383 K). To have further insight into the transformation, a similar reaction was carried out with a di-ortho-substituted aniline like 2,6-dimethylaniline in place of unsubstituted aniline. A complex **3c** analogous to **3a** and **3b** was obtained. The result clearly indicates that dimerization of coordinated *cis*-anilines in **1-Cl** via *o*-C$_{arom}$—N bond fusion occurs only when benzene is substituted by the aromatic amines.

Details of the chemical reactions are submitted as Supporting Information. Microanalytical, positive-ion electrospray ionization mass spectrometry (ESI-MS) spectra, together with NMR spectral data of the compounds **1-Cl**, **2-Cl**, and **3**, convincingly support their formulations as shown in the above schemes. Characterization data of the products are submitted as Supporting Information (Figures S1—S17). Their identities were finally confirmed by determination of the three-dimensional X-ray structures of the representative complexes (Figures S18—S20 and Tables S1 in the Supporting Information). For example, the chloro-substituted complex **3b** formed a suitable crystal for X-ray structure determination. However, the physicochemical properties of the other two complexes **3a** and **3c** are similar to those of the above chloro derivative.

Molecular views and selected structural parameters of the complexes **1a-Cl** and **2-Cl** are shown in Figure 1 and that of the compound **3b** are displayed in Figure 2. The bond parameters exhibit the following trend: for **2-Cl**, the values for C═NH (1.331 Å), C═NPh (1.336 Å), and C═C(meta) bond lengths at 1.360 Å, and for the compound **3**, the values for C═NH (1.331 Å),
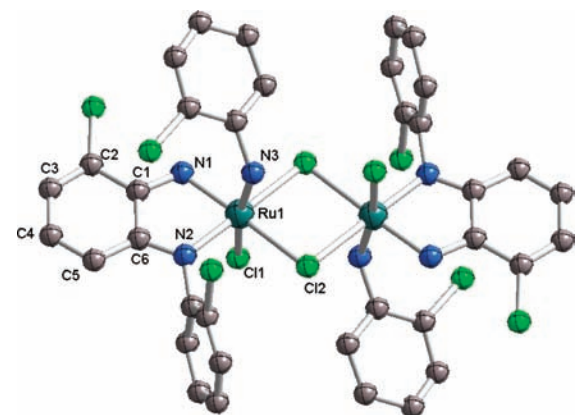

Figure 2. Molecular view of the complex **3b**. Hydrogen atoms are omitted for clarity. Selected bond lengths: Ru1—N1, 1.953(2); Ru1—N2, 1.988(2); Ru1—N3, 2.152(2); C1—N1, 1.332(3); C2—C1, 1.422(3); C3—C2, 1.356(4); C4—C3, 1.441(5); C5—C4, 1.351(5); C6—C5, 1.422(3) C6—N2, 1.331(3); N2—C7, 1.445(3).

C═NPh (1.332 Å), and C═C(meta) bond lengths at 1.355A. This trend in the bond parameter is very similar to our previously reported results indicating an *o*-semiquinonediimine rather than an *o*-quinonediimine formulation for the coordinated ligands.[13] The compounds are diamagnetic at room temperature. This is ascribed[13,14] to strong antiferromagnetic interactions between the unpaired spins on the ligand and the trivalent ruthenium centers.

To probe the oxidation state of the coordinated bidentated semidine ligand in these two complexes, we examined their redox behaviors. The voltammogram of **2-Cl** displays one reversible

oxidation at 1.05 V in addition to an irreversible reduction feature at -0.85 V in the potential range from $+1.5$ to -1.5 V (Figure S21 in the Supporting Information), while the voltammograms of **3** showed one irreversible reduction near about -0.75 V and an irreversible oxidation near about 0.65 V. The reversible oxidative response of **2-Cl** was studied by electron paramagnetic resonance (EPR) spectroscopy. Oxidative electrolysis of the complex in dichloromethane at 77 K yielded a ligand-based signal at $g = 1.998$, signifying the generation of a ruthenium(IV) semiquinonediimine radical[15] complex upon oxidation. The EPR spectrum of $[2]^{2+}$ is submitted as Figure S22 in the Supporting Information.

The detailed mechanism of the reaction remains unresolved as yet. We have not been able to identify or isolate the intermediates of the above reactions. It is worth noting that C—N bond-fusion reactions do not occur under anaerobic conditions. Thus, we conclude that an oxidizable metal-mediator complex with participation of air brings about this transformation. The chemical reaction of CpRu^{II}Cl(PPh$_3$)$_2$ with aniline under anaerobic conditions resulted in a mixture of products, as evidenced from ESI-MS analysis of the crude product.

In summary, the present results have clearly demonstrated that low-valent metal complexes with oxidizable character can act as excellent mediators for o-C$_{arom}$—N bond-making reactions in anilido substrates. Such a mediator is more preferable because of its labile nature, which is crucial for cis coordination of aniline to the mediator complex. Thus, the redox-inert areneruthenium(II) complex (Bnz)$_2$Ru^{II}$_2$Cl$_4$ failed to bring about C$_{arom}$—N bond-fusion reaction, while the oxidizable complex CpRu^{II}Cl(PPh$_3$)$_2$ mediated the reaction successfully. However, the Bnz ligand in **1-Cl** upon substitution became susceptible to oxidation and freely mediated oxidative C—N bond-formation reactions. Studies on similar reactions using other suitable metal-mediator complexes and substituted anilines are in progress.

■ ASSOCIATED CONTENT

⑤ **Supporting Information.** X-ray crystallographic data in CIF format, experimental details of the compounds **1-Cl**, **2-Cl**, and **3** along with their spectra and ORTEP diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: icsg@iacs.res.in.

■ ACKNOWLEDGMENT

■ REFERENCES

(1) (a) Godula, K.; Sames, D. *Science* **2006**, *312*, 67. (b) Cho, S. H.; Kim, J. Y.; Lee, S. Y.; Chang, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 9127.

(2) (a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (b) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (c) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338.

(3) (a) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (b) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534. (c) Phipps, R. J.; Gaunt, M. J. *Science* **2009**, *323*, 1593.

(4) (a) Hili, R.; Yudin, A. K. *Nat. Chem. Biol.* **2006**, *2*, 284.(b) *Amino Group Chemistry, From Syntheses to the Life Science*; Ricci, A., Ed.; Wiley-VCH: Weinheim, Germany, 2007. (c) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lamire, M. *Chem. Rev.* **2002**, *102*, 1359.

(5) Li, D.; Huang, J.; Kaner, R. B. *Acc. Chem. Res.* **2009**, *42*, 135 and references cited therein.

(6) (a) Zhang, X.-X.; Sadighi, J. P.; Mackewitz, T. W.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 7606.(b) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F. Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcacer, L., Ed.; Reidel: Dordrecht, The Netherlands, 1987; pp 105—120. (c) Gospodinova, N.; Terlemezyan, L. *Prog. Polym. Sci.* **1998**, *23*, 1443.

(7) Finar, I. L. *Organic Chemistry*, 6th ed.; Addison-Wesley: Reading, PA, 1973; Vol. 1, p 685.

(8) Samanta, S.; Goswami, S. *J. Am. Chem. Soc.* **2009**, *131*, 924.

(9) (a) Mitra, K. N.; Goswami, S. *Chem. Commun.* **1997**, 49. (b) Mitra, K. N.; Majumder, P.; Peng, S.-M.; Castiñeiras, A.; Goswami, S. *Chem. Commun.* **1997**, 1267. (c) Mitra, K. N.; Peng, S.-M.; Goswami, S. *Chem. Commun.* **1998**, 1685. (d) Majumder, P.; Falvello, L. R.; Tomàs, M.; Goswami, S. *Chem.—Eur. J.* **2001**, *7*, 5222. (e) Das, C.; Goswami, S. *Comments Inorg. Chem.* **2003**, *24*, 137. (f) Mitra, K. N.; Choudhury, S.; Castiñeiras, A.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1998**, 2901. (g) Mitra, K. N.; Goswami, S. *Inorg. Chem.* **1997**, *36*, 1322. (h) Samanta, S.; Adak, L.; Jana, R.; Mostafa, G.; Tuononen, H. M.; Ranu, B. C.; Goswami, S. *Inorg. Chem.* **2008**, *47*, 11062.

(10) (a) Soper, J. D.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 5594. (b) Soper, J. D.; Saganic, E.; Weinberg, D.; Hrovat, D. A.; Benedict, J. B.; Kaminsky, W.; Mayer, J. M. *Inorg. Chem.* **2004**, *43*, 5804. (c) Bai, G.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 1856.

(11) Hoover, J. M.; DiPasquale, A.; Mayer, J. M.; Michael, F. E. *Organometallics* **2007**, *26*, 3297 and references cited therein.

(12) Dougan, S. J.; Melchart, M.; Habtemariam, A.; Parsons, S.; Sadler, P. J. *Inorg. Chem.* **2006**, *45*, 10882.

(13) Chatterjee, S.; Singh, P.; Fiedler, J.; Baková, R.; Záliš, S.; Kaim, W.; Goswami, S. *Dalton Trans.* **2009**, 7778.

(14) Samanta, S.; Singh, P.; Fiedler, J.; Záliš, S.; Kaim, W.; Goswami, S. *Inorg. Chem.* **2008**, *47*, 1625.

(15) Chłopek, K.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2005**, *44*, 7087.

3173

dx.doi.org/10.1021/ic101868w |*Inorg. Chem.* 2011, 50, 3171–3173