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C–N Bond Cleavage of Anilines by a (Salen)ruthenium(VI) Nitrido Complex

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Supporting Information

ABSTRACT: We report experimental and computational studies of the facile oxidative C–N bond cleavage of anilines by a (salen)ruthenium(VI) nitrido complex. We provide evidence that the initial step involves nucleophilic attack of aniline at the nitrido ligand of the ruthenium complex, which is followed by proton and electron transfer to afford a (salen)ruthenium(II) diazonium intermediate. This intermediate then undergoes unimolecular decomposition to generate benzene and N_2.

Complexes containing metal–nitrogen multiple bonds are an important class of compounds because of their roles in nitrogen fixation, nitrogenation reactions, and catalysis.[1,2] Osmium(VI) nitrido complexes containing nitrogen-based ligands such as *cis*- or *trans*-$[Os^{VI}(N)(tpy)Cl_2]^+$ (tpy = 2,2′:6′,2″-terpyridine), $[Os^{VI}(N)(tpm)Cl_2]^+$ [tpm = tris(1-pyrazolyl)methane], $[Os^{VI}(N)(Tp)Cl_2]$ [Tp = hydrotris(1-pyrazolyl)borate], and $[Os^{VI}(N)(bpy)Cl_3]$ (bpy = 2,2′-bipyridine) have been shown to exhibit novel electrophilic properties.[3–5] We recently reported a highly electrophilic (salen)ruthenium(VI) nitrido complex, $[Ru^{VI}(N)(L)(MeOH)](PF_6)$ [**RuN**; L is the cyclohexylene-bridged salen ligand *N,N*′-bis(salicylidene)-*o*-cyclohexylenediamine dianion], that reacts readily with various nucleophiles such as aliphatic secondary amines,[6] thiols,[7] and isocyanides.[8] It is also capable of transferring its N atom to alkenes to give aziridines[9] and activating the strong C–H bonds of alkanes.[10] We report herein that **RuN** can be used for facile oxidative C–N bond cleavage of anilines under ambient conditions.

There have been several reports on transition-metal-mediated cleavage of aliphatic C–N bonds.[11] On the other hand, there is only one example of the activation of the relatively inert C–N bonds of anilines under mild conditions: $(^tBu_3SiO)_3Ta$ undergoes oxidative addition of the C–N bond of *p*-$CF_3C_6H_4NH_2$ at room temperature to afford $(^tBu_3SiO)_3(H_2N)Ta(p\text{-}C_6H_4CF_3)$.[12] Catalytic C–C bond formation reactions proceeding via cleavage of C–N bonds in aniline derivatives through catalysis by the ruthenium complex $RuH_2(CO)(PPh_3)_3$ have also been reported,[13] but these reactions require high temperature (120 °C).

Addition of excess aniline (>100 equiv) to **RuN** in CH_2Cl_2 at 23 °C under argon resulted in a rapid color change from orange to red. Electrospray ionization mass spectrometry (ESI-MS) analysis of the red solution showed two cationic ruthenium peaks at *m/z* 608 and 620 (Figure 1a), which are assigned to $[Ru(L)(NH_2Ph)_2]^+$ and $[Ru(L)(N_2Ph)(NH_2Ph)]^+$, respectively. When 50% ^{15}N-labeled **RuN** (**Ru^{15}N**) was reacted with unlabeled aniline, a similar mass spectrum was obtained, but careful examination of the peak at *m/z* 620 revealed that the three N atoms consist of 0.5 ^{15}N and 2.5 ^{14}N, indicating that one of the N atoms is derived from the nitrido ligand (Figure 1b). On the other hand, the peak at *m/z* 608 did not contain any ^{15}N.

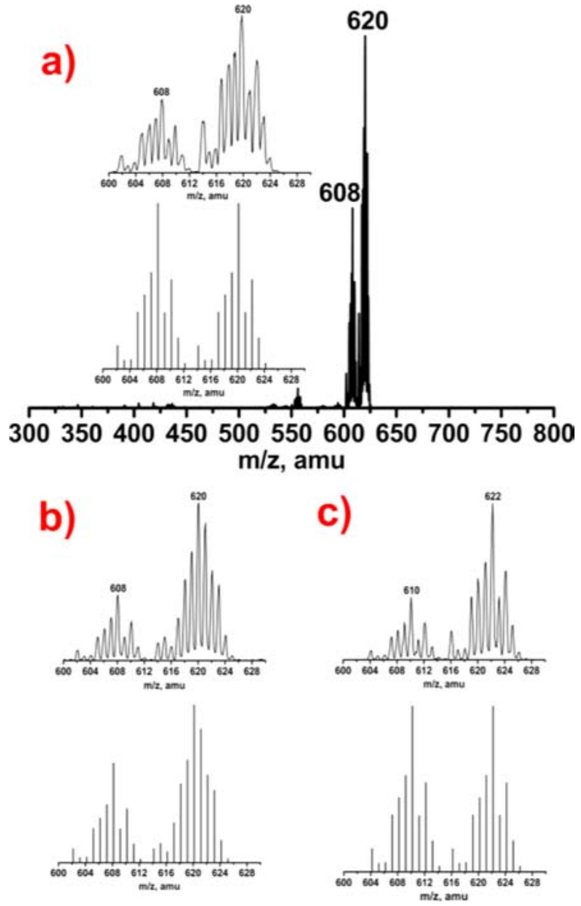

Figure 1. (a) ESI-MS data for the reaction mixture of **RuN** (50 μM) and aniline (0.01 M) in CH_2Cl_2 taken after 2 min. Insets show the expanded and simulated patterns of the peaks at *m/z* 608 and 620. (b, c) Same as in the insets in (a), except that (b) 50% **Ru^{15}N** or (c) 98% (^{15}N)aniline was used.

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However, when unlabeled **RuN** was reacted with (^{15}N)aniline, the ESI-MS data showed that both peaks at m/z 608 and 620 were shifted to higher mass by m/z 2, indicating that both species contain two N atoms derived from aniline (Figure 1c). On standing, the relative intensity of the peak at m/z 608 increased while that of the m/z 620 peak decreased, with a concomitant change in the solution color from red to green; this suggested that the diazonium species $[Ru(L)(N_2Ph)(NH_2Ph)]^+$ decomposed to $[Ru(L)(NH_2Ph)_2]^+$ (in the presence of $PhNH_2$), which is a known green complex.[14]

The IR spectrum of the red solution exhibited a broad peak at 1833 cm^{-1}, which was assigned to the ν(NN) stretch of the diazonium complex. This peak shifted to the expected wavenumber of 1798 cm^{-1} when (^{15}N)aniline was used [Figure S1 in the Supporting Information (SI)].

Analysis of the final green solution by gas chromatography (GC) and GC−MS indicated the presence of benzene (0.36 ± 0.03 equiv based on **RuN**). No biphenyl was detected. Similarly, toluene, anisole, and chlorobenzene were detected in similar yields when *p*-methylaniline, *p*-methoxyaniline, and *p*-chloroaniline, respectively, were used as the substrate. N_2 production was also detected in these reactions but was not quantified.

The ESI-MS and GC−MS results suggested that aniline reacts with **RuN** via attack at the nitrido ligand to generate the ruthenium(II) diazonium complex $[Ru(L)(N_2Ph)(NH_2Ph)]^+$, which then decomposes to the bis(aniline)ruthenium(III) complex $[Ru(L)(NH_2Ph)_2]^+$, benzene, and N_2. These reactions result in an overall C−N bond cleavage of aniline. This is in contrast to the reaction of aliphatic secondary amines with **RuN**, which generate stable ruthenium(IV) hydrazido complexes without C−N bond cleavage.[6]

Attempts to isolate the diazonium complex were unsuccessful; only the reported $[Ru(L)(NH_2Ph)_2]^+$ complex could be obtained as the PF_6^- salt.[14] However, when the reaction of **RuN** with aniline was carried out in the presence of $^nBu_4NCl$, the diazonium complex $[Ru(N_2Ph)(L)Cl]$ was isolated in 30% yield as a stable red crystalline solid. The complex is diamagnetic, as evidenced by well-resolved ^{1}H NMR signals at normal fields in CD_2Cl_2. The two imine protons of the salen ligand occur as singlets at 8.35 and 8.28 ppm. In the IR spectrum, the two strong peaks at 1799 and 1776 cm^{-1} are assigned to the multiple ν(NN) stretching bands of the diazonium ligand.[15] The molecular structure of $[Ru(N_2Ph)(L)Cl]$ was determined by X-ray crystallography (Figure 2; the crystal data and structure refinement details are given in Table S1 in the SI). It has a distorted octahedral geometry in which the Ru atom is surrounded by two O and two N atoms of the salen ligand in the equatorial plane and the axial positions are occupied by one chloro ligand and one phenyldiazo ligand (N_2Ph). The Ru−N3 [1.784(4) Å] and N3−N4 [1.172(6) Å] bond distances and the Ru−N3−N4 [169.1(4)°] and N3−N4−C21 [130.1(5)°] bond angles are comparable to those of $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ [1.796(6) and 1.144(10) Å and 171.2(9) and 135.9(11)°, respectively].[16]

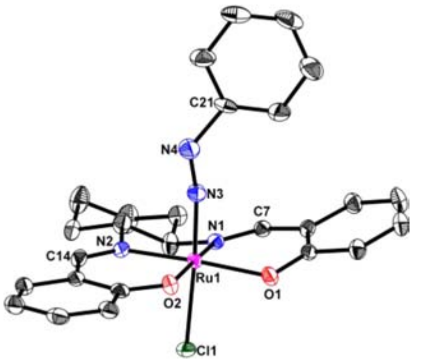


Figure 2. Molecular structure of $[Ru(N_2Ph)(L)Cl]\cdot 2CH_2Cl_2$. Thermal ellipsoids are drawn at 50% probability. H atoms and solvent molecules have been omitted for clarity.

The kinetics of the reaction of **RuN** with $PhNH_2$ were studied by UV−vis spectrophotometry. The spectral changes in dichloroethane at 298.0 K show that this reaction consists of three well-separated phases (Figure 3a−c). The final UV−vis spectrum is very similar to that of $[Ru^{III}(L)(NH_2Ph)_2]^+$ (Figure S2). The kinetics of the first phase was studied under pseudo-first-order conditions (Figure 3d). The reaction is first order in [**RuN**] and second order in [aniline] with a third-order rate constant k_3 = (2.60 ± 0.05) × 10 M^{-2} s^{-1}. The reaction rate is sensitive to substituents at the para position of the aniline (p-X-$PhNH_2$). A linear Hammett correlation between $\log(k_{obs}^{X}/k_{obs}^{H})$ and σ_p was found (Figure S3), with the reaction constant $\rho = -(6.57 \pm 0.35)$, consistent with nucleophilic attack of $PhNH_2$ at the nitrido ligand of **RuN**. The second phase (Figure S4) is first order in both [**RuN**] and [aniline] with a second-order rate constant k_2 = (5.76 ± 0.16) × 10^{-1} M^{-1} s^{-1}. The third phase (Figure S5) is independent of [$PhNH_2$] (0.1−0.4 M) with a first-order rate constant k = (3.98 ± 0.08) × 10^{-3} s^{-1}. No kinetic isotopic effect (KIE) was found for the first two steps when aniline-d_7 was used (KIE = 0.98 ± 0.03 and 1.04 ± 0.02 for the first and second step, respectively) (Figures S6 and S7). There was no difference between the rate constants obtained in air or under argon.

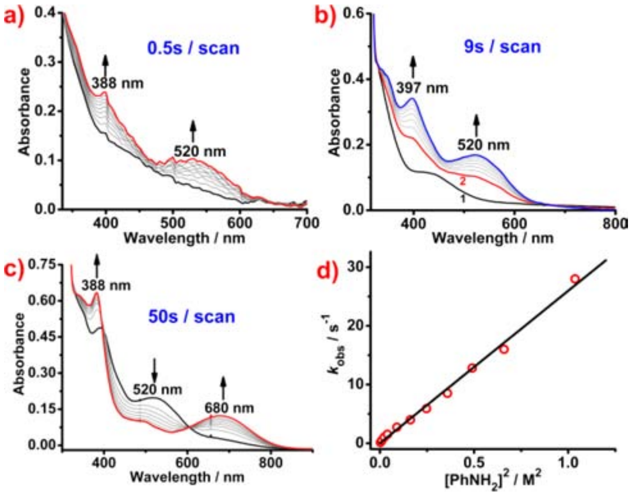
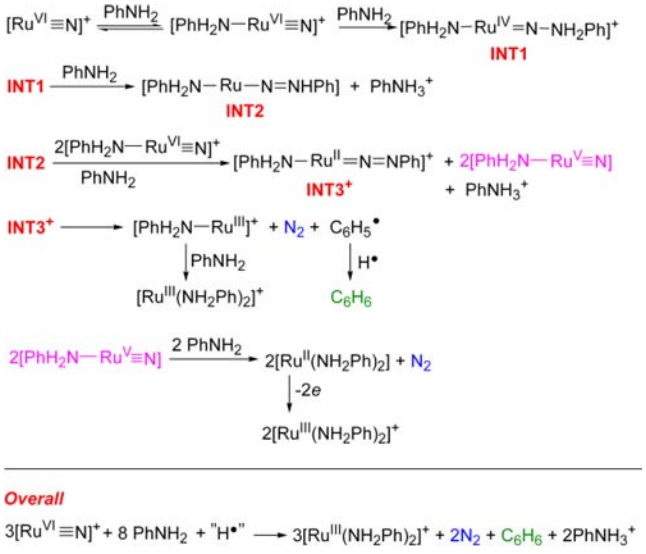


Figure 3. UV−vis spectral changes for the reaction of **RuN** with $PhNH_2$ in dichloroethane at 298.0 K. [**RuN**] = 5.0 × 10^{-5} M; [$PhNH_2$] = 0.1 M. (a) First phase. (b) Second phase: (1) before mixing; (2) immediately after mixing. (c) Third phase. (d) Plot of k_{obs} vs $[PhNH_2]^2$ for the first phase: slope = (2.60 ± 0.05) × 10; y-intercept = (5.21 ± 0.01) × 10^{-3}; r^2 = 0.9936.

On the basis of the kinetic studies and product analysis, a proposed mechanism for the reaction of **RuN** with $PhNH_2$ is shown in Scheme 1. The first step involves equilibrium coordination of a $PhNH_2$ molecule to $[Ru^{VI}(N)(L)]^+$ to give $[Ru^{VI}(N)(L)(NH_2Ph)]^+$, which activates the complex toward nucleophilic attack at the nitrido ligand by a second $PhNH_2$

Scheme 1. Proposed Mechanism for the Reaction of RuN with Aniline (the Salen Ligand Has Been Omitted for Clarity)



molecule to generate a ruthenium(IV) hydrazido complex, $[Ru^{IV}(N{-}NH_2Ph)(L)(NH_2Ph)]^+$ (**INT1**). This is consistent with the observed first kinetic phase, which is first order in [**RuN**] and second order in $[PhNH_2]$. Equilibrium binding of other ligands such as pyridine to $[Ru^{VI}(N)(L)]^+$ has been observed.[9,10]

In the second step, initial rate-limiting proton transfer from $[Ru^{IV}(N{-}NH_2Ph)(L)(NH_2Ph)]^+$ to $PhNH_2$ to afford **INT2** is proposed. This would be followed by rapid transfer of two electrons and one proton to generate the ruthenium(II) diazonium complex $[Ru^{II}(L)(N_2Ph)(NH_2Ph)]^+$ (**INT3**$^+$). This step corresponds to the observed second kinetic phase, which is first order in $[Ru^{VI}]$ and $[PhNH_2]$. $PhNH_3^+$ was observed by ESI-MS. No KIE was observed for this proposed step, but a small KIE (within a factor of 2) has been reported for other proton transfer reactions, such as proton transfer from $[Al(OH_2)_6]^{3+}$ to H_2O.[17]

The final step involves initial rate-limiting unimolecular decomposition of $[Ru^{II}(L)(N_2Ph)(NH_2Ph)]^+$ to generate $[Ru^{III}(L)(NH_2Ph)]^+$, N_2, and $C_6H_5^\bullet$. $[Ru^{III}(L)(NH_2Ph)]^+$ then rapidly picks up a $PhNH_2$ molecule to give the product $[Ru^{III}(L)(NH_2Ph)_2]^+$. The phenyl radical abstracts a hydrogen atom to give benzene in 36 ± 3% yield. The yield of benzene decreased to 22% when the reaction was carried out in air instead of under argon. Also, when the reaction was carried out in the presence of $BrCCl_3$, PhBr was detected in 29% yield. These observations are consistent with the intermediacy of $C_6H_5^\bullet$. When the reaction was carried out in CD_2Cl_2 as the solvent, both C_6H_6 and C_6H_5D were detected, and when the reaction was carried out in CH_2Cl_2 using aniline-d_7 as the substrate, both C_6D_6 and C_6D_5H were detected. These observations indicate that $C_6H_5^\bullet$ abstracts a hydrogen atom from either the solvent or aniline/anilinium to generate C_6H_6. One-electron reduction of $[Ru^{VI}(N)(L)(NH_2Ph)]^+$ in the second step generates a ruthenium(V) nitride, which could undergo facile bimolecular N···N coupling to release N_2 and $[Ru^{II}(L)(NH_2Ph)_2]$ in the presence of excess $PhNH_2$.[14] The latter species may be oxidized by radicals derived from solvent or aniline or by trace air (E^0 for $[Ru^{III}(PhNH_2)_2(L)]^+$ is −0.86 V vs $Cp_2Fe^{+/0}$)[14] to give the final product, $[Ru^{III}(L)(NH_2Ph)_2]^+$. Analysis by UV−vis spectrophotometry indicated that $[Ru^{III}(L)(NH_2Ph)_2]^+$ was produced quantitatively. In the overall reaction, 3 mol of **RuN** reacts with excess aniline to give 3 mol of $[Ru^{III}(L)(NH_2Ph)]^+$, 2 mol of N_2, and 1 mol of benzene.

According to Scheme 1, half of the N_2 produced should come from decomposition of the diazonium complex and the other half from N···N coupling of $(PhH_2N)Ru^V{\equiv}N$. To verify this, we performed the reaction of 50% ^{15}N-labeled **Ru^{15}N** with excess (^{15}N)aniline in dichloroethane and analyzed the isotopic distribution of the N_2 produced by GC−MS. The N_2 produced

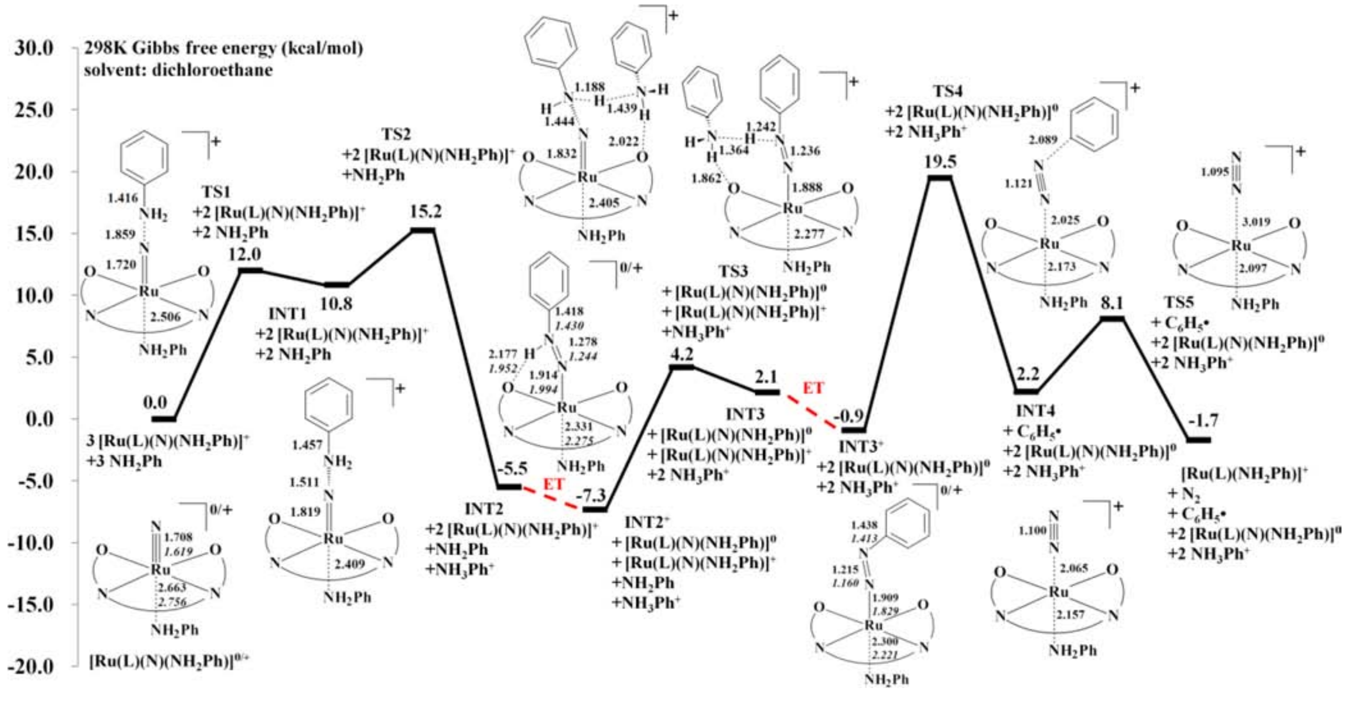


Figure 4. Free energy surface for the reaction of $[Ru^{VI}(N)(L)(NH_2Ph)]^+$ with aniline. Relative Gibbs free energies at 298 K in dichloroethane are given in kcal mol^{-1}. Selected bond lengths are given in Å; the values in italic font are for the cations $[Ru(N)(L)(NH_2Ph)]^+$, **INT2**$^+$, and **INT3**$^+$.

was found to consist of 18% $^{14}N^{14}N$, 46% $^{14}N^{15}N$, and 36% $^{15}N^{15}N$ (±3%) after background correction.[18] This finding is in reasonable agreement with the calculated values of 13% $^{14}N^{14}N$, 50% $^{14}N^{15}N$, and 37% $^{15}N^{15}N$ for N_2 derived equally from diazonium decomposition and N···N coupling. If N_2 were obtained exclusively from N···N coupling, the isotopic composition would be 25% $^{14}N^{14}N$, 50% $^{14}N^{15}N$, and 25% $^{15}N^{15}N$. On the other hand, if N_2 were obtained only from cleavage of the C−N bond in the diazonium complex, the expected distribution would be 50% $^{14}N^{15}N$ and 50% $^{15}N^{15}N$.

Density functional theory calculations were performed to gain more insight into the mechanism of cleavage of the C−N bond in $PhNH_2$ by **RuN** (Figure 4). In the first step, attack of an aniline molecule at the nitrido ligand of $[Ru^{VI}(N)(L)(NH_2Ph)]^+$ forms the ruthenium(IV) hydrazido complex $[Ru(N{-}NH_2Ph)(L)(NH_2Ph)]^+$ (**INT1**) via **TS1** with a barrier height ($\Delta G^{\ddagger}_{298}$) of 12.0 kcal mol^{-1}. In this complex, the N−N distance is 1.511 Å, and the Ru−N bond is elongated from 1.619 to 1.819 Å. **INT1** then undergoes a proton transfer to another aniline via **TS2** to form $[Ru(N{-}NHPh)(L)(NH_2Ph)]^0$ (**INT2**) and protonated aniline, $[PhNH_3]^+$. The barrier height of **TS2** is 15.2 kcal mol^{-1} relative to $[Ru^{VI}(N)(L)(NH_2Ph)]^+ + 2PhNH_2$. This proton transfer process was confirmed by natural bond orbital analysis.[19] Compared with **INT1**, the N−N distance in **INT2** is reduced by ca. 0.23 Å and the Ru−N bond is slightly increased by 0.1 Å to 1.914 Å. Electron transfer (ET) between **INT2** and $[Ru(N)(L)(NH_2Ph)]^+$ then occurs, producing **INT2**$^+$ and $[Ru(N)(L)(NH_2Ph)]^0$. **INT2**$^+$ undergoes a second proton transfer to aniline to generate $[Ru(N{-}NPh)(L)(NH_2Ph)]^0$ (**INT3**) via **TS3** ($\Delta G^{\ddagger}_{298}$ = 11.5 kcal mol^{-1} relative to **INT2**$^+$ + $PhNH_2$). Unlike the first proton transfer, the N−N and Ru−N bonds in **INT3** are only slightly decreased by ca. 0.03 and 0.08 Å, respectively. Subsequently, a second ET between **INT3** and $[Ru(N)(L)(NH_2Ph)]^+$ occurs, yielding the ruthenium(II) diazonium complex $[Ru(L)(N_2Ph)(NH_2Ph)]^+$ (**INT3**$^+$) and $[Ru(N)(L)(NH_2Ph)]^0$. **INT3**$^+$ then undergoes C−N bond cleavage to give $C_6H_5^{\bullet}$ and $[Ru(L)(N_2)(NH_2Ph)]^+$, which is followed by loss of N_2 from the latter species.

In summary, we have reported the first example of oxidative C−N bond cleavage of anilines by a nitrido complex under ambient conditions. Mechanistic studies suggested that the initial step involves nucleophilic attack of aniline on the nitride. This is followed by proton and electron transfer to generate a diazonium species, which then undergoes unimolecular decomposition to generate benzene and N_2.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, crystal data, and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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