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Molecular Editing

A Synthetic Cycle for Heteroarene Synthesis by Nitride Insertion**

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Abstract: Recent interest in skeletal editing necessitates the continued development of reagent classes with the ability to transfer single atoms. Terminal transition metal nitrides hold immense promise for single-atom transfer, though their use in organic synthesis has so far been limited. Here we demonstrate a synthetic cycle with associated detailed mechanistic studies that primes the development of terminal transition metal nitrides as valuable single-atom transfer reagents. Specifically, we show [*cis*-terpyOsNCl$_2$]PF$_6$ inserts nitrogen into indenes to afford isoquinolines. Mechanistic studies for each step (insertion, aromatization, product release, and nitride regeneration) are reported, including crystallographic characterization of diverted intermediates, kinetics, and computational studies. The mechanistic foundation set by this synthetic cycle opens the door to the further development of nitrogen insertion heteroarene syntheses promoted by late transition metal nitrides.

*H*omogeneous transition-metal-catalyzed nitrene transfer to organic substrates is a remarkably useful strategy to synthesize high value nitrogen-containing compounds including aziridines, pyrroles, and amines.[1–11] Typically, these reactions occur via the intermediacy of terminal metal imido or metallonitrenoid species.[12–17] By contrast, nitrogen transfer from terminal metal nitrido complexes is much less explored despite their unique and often attractive reactivity.[12,14,18–21] Indeed, only recently has the first example of catalytic nitrogen atom transfer to organic substrates from a well-characterized terminal metal nitride been reported.[22] Instead, the majority of studies on terminal metal nitrides focus on N$_2$ reduction and valorization by early transition metals.[23–30] These early metal nitrides are typically nucleophilic at N due to polarization of the HOMO away from the relatively high energy metal d-orbitals.[31] By the same analysis, group 8 metal nitrides often behave as electrophiles at nitrogen[32] and have shown distinct stoichiometric reactivity with potential for remarkable utility in synthetic organic chemistry.

Meyer's seminal work on cationic osmium(VI) nitrides ignited interest in this area by demonstrating their reactivity with a variety of nucleophiles (eg. PPh$_3$, N$_3^-$, RSH, etc.).[33] Subsequently, Mayer extended this reactivity to organic nucleophiles, including nitrogen insertion to B–C bonds.[34–36] Additionally, Lau has demonstrated the propensity for cationic ruthenium(VI) nitrides to perform aziridinations and C–H activations in the presence of pyridine.[37,38] The same group has more recently reported photochemical C–H activation by an anionic osmium(VI) nitride.[39] The present report was inspired in particular by reports from the Brown group, demonstrating that cationic, terminal osmium(VI) nitrido complexes can insert nitrogen into conjugated olefins (Figure 1A).[40,41]

With this precedent in mind, we envisioned analogous N-atom insertion to cyclic olefins as an attractive route to heterocycles upon aromatization of the intermediate azaallenium species.[42] We report here the successful realization of

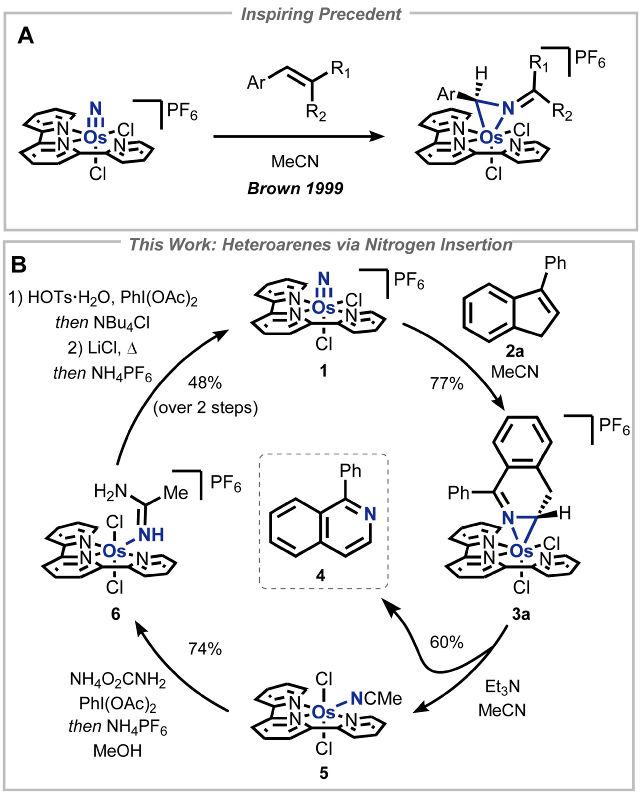

Figure 1. a) Inspiring, unique reactivity of group 8 metal nitrides. b) Synthetic cycle for N-atom insertion into phenylindene.

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a 5-step synthetic cycle which enables the formal insertion of a nitrogen atom into an indene and regeneration of the parent osmium nitride (Figure 1B). Below, the development of this cycle and mechanistic aspects elucidated along each step are discussed.

While previous reports have demonstrated that 6- and 7-membered cyclic olefins can undergo N-atom insertion, cyclopentadiene was previously reported by Brown as an unsuccessful substrate.[43] In spite of these reports, our initial studies exploring the reactivity of [*cis*-terpyOsNCl$_2$]PF$_6$ (**1**) showed that aryl-substituted indenes were productive (the parent indene only reacts at higher temperature and does not give diagmagnetic products). As such, 3-phenyl-1*H*-indene (**2a**) was chosen as a model substrate. Heating **1** at 50 °C in the presence of excess **2a**, we observed a modest yield (27 %) of the expected insertion product 1-phenylisoquinoline. When the reaction was instead conducted at ambient temperature, the azaallenium **3a** could be isolated by precipitation with Et$_2$O in 77 % yield (Figure 2A). ^{1}H NMR analysis indicates a doublet of doublets at δ 6.25 ppm, which corresponds to the OsC*H*, split by the diastereotopic set of methylene protons. HSQC indicates this proton is coupled to an sp^3 carbon with δ 42.9 ppm, which we assign to Os*C*H in agreement with precedent.[40,41] Attempts to crystallize this structure from MeCN solutions resulted in spontaneous aromatization of the azaallenium ligand with loss of HCl to afford [(terpy)OsCl(NCMe)(1-phenylisoquinoline)]PF$_6$ (**7**). In weakly-coordinating solvents, crystals suitable for X-ray diffraction could not be grown under inert atmosphere, and only yielded crystalline material upon exposure to air, affording the analogous aromatized Os^{III} isoquinoline complex (see Supporting Information).

With the goal of disfavoring aromatization to obtain crystallographic evidence for the azaallenium, we replaced **2a** with 1,1-dimethyl-3-phenylindene (**2f**, Figure 2B). Sur-

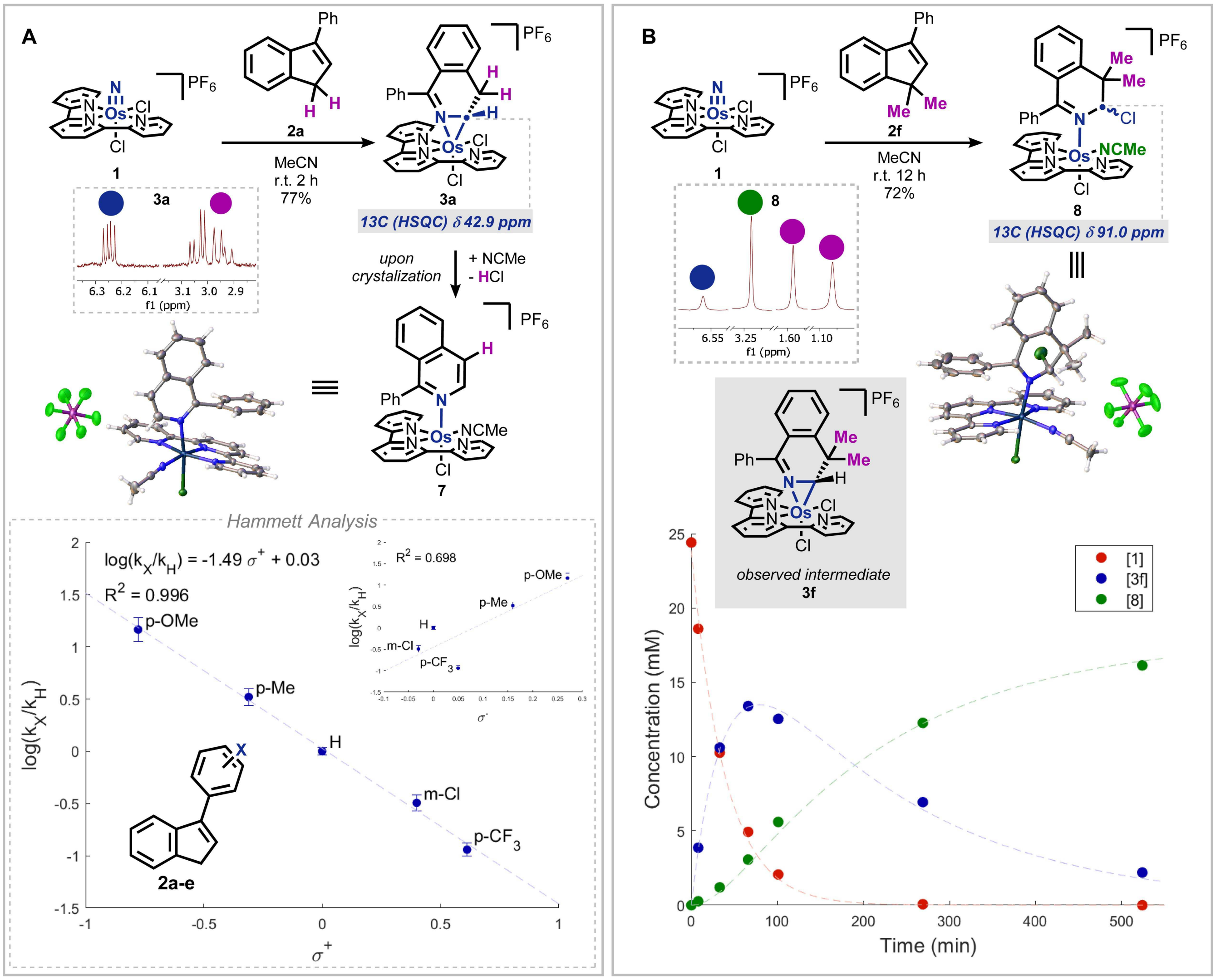

Figure 2. a) Reaction of **2a** with **1**, NMR evidence for azaalenium **3a**, crystallographic characterization of aromatized product, and Hammett study of reaction rate (separate-pot, pseudo-first-order k_{obs}, $n=3$). b) Reaction of **2f** with **1**, crystallographically characterized azaallyl chloride **9**, and kinetic data at 25 °C indicating formation of intermediate **3f**, fit to an A→B→C model.

prisingly, rather than affording an analogous azaallenium, **1** reacts cleanly with **2f** to afford a crystallographically characterized aza-allyl chloride (**8**). HSQC confirms that the singlet in the ^{1}H NMR spectrum assigned to CCl*H* (δ 6.58 ppm) is coupled to a strongly deshielded sp^3 carbon at δ 91 ppm, which diverges substantially from both **3a** and from previously reported azaallenium complexes, instead aligning more closely with previously reported N-chloroalkylpyridinium salts.[44] Density functional theory (DFT) modeling of the azaallenium energies at the B3LYP-D3/6-311+g(d,p)-(C,H,N,Cl)/SDD(Os)-PCM(MeCN)//B3LYP-D3/6-31g(d)-(C,H,N,Cl)/SDD(Os)-PCM(MeCN) level of theory show a stark decrease in stability of the azaallenium isomer relative to the aza-allyl chloride upon introduction of the methyl groups, presumably due to steric clashes between the methyl groups and the equatorial ligands (see Supporting Information for details).

These observations raise a mechanistic question regarding the primacy of either the azaallenium or azaallyl chloride on the reaction coordinate. Based on the observed displacement of chloride upon attempted crystallization of **3a**, we hypothesized that the aza-allyl chloride **8** results from solvolysis of **3f**. Indeed, monitoring the reaction of **1** with **2f** by NMR indicates the buildup of an intermediate which we tentatively assign as the dimethylated azaallenium **3f**. This species quickly decomposes to give **8** prior to full consumption of the starting material. **3f** builds to a maximum total concentration at approximately 80 % conversion of **1**, at which point **3f** and **8** were observed in 69 % and 13 % yield respectively (representing 88 % of total mass balance), and the kinetic behavior was well-approximated by a pseudo-first order A→B→C model with roughly five-fold faster consumption of **1** than of **3f**. By contrast, reaction of **1** with **2a** directly affords the azaallenium **3a** in 95 % yield by NMR with no observable intermediates. Both reactions exhibit first order kinetics in **1** under pseudo-zero order concentrations of **2**. The reaction with **2a** is unsurprisingly faster than with **2f** likely due to increased sterics around the olefin.

To better elucidate the mechanism for the formation of **3**, we conducted a Hammett analysis by varying the substituent on the aryl group (Figure 2A). The strong correlation between reaction rate and σ^+ ($\rho = -1.5$, $R^2 = 0.996$) supports carbocation character developing at the doubly benzylic position.[45,46] We interpret the relatively small ρ as indicative of a strongly asynchronous aziridination with significant charge distribution throughout the complex in the transition state rather than as evidence for radical character on the basis of the far poorer correlation with Creary's $\sigma^\bullet$ scale ($R^2 = 0.698$).[47]

Modeling of the reaction sequence from **1** to **3a** by Density functional theory (DFT) agrees with this experimental assessment and predicts an aziridination-electrocyclic ring opening sequence (Figure 3). Direct nucleophilic attack of the olefin at the nitride ligand proceeds with a modest energy barrier (**TS1**) to a carbocation-like intermediate (**INT1**), in agreement with our Hammett analysis. Ring-closing completes the stepwise aziridination to give **INT2**.[38] Because **TS1** and **TS2** are very similar in predicted energy, we do not interpret this definitively supporting a stepwise aziridination mechanism. Indeed, rate determining ring-closure or asynchronous, concerted aziridination are also consistent with the observed electronic trend. C–C bond cleavage can proceed through **TS3** (reminiscent of haloaziridine electrocyclic ring opening)[48,49] to give the unobserved azaallenium isomer **3a***. This species can isomerize to the observed, more stable isomer **3a** through an "allene-rock" mechanism.[41] Our calculations additionally

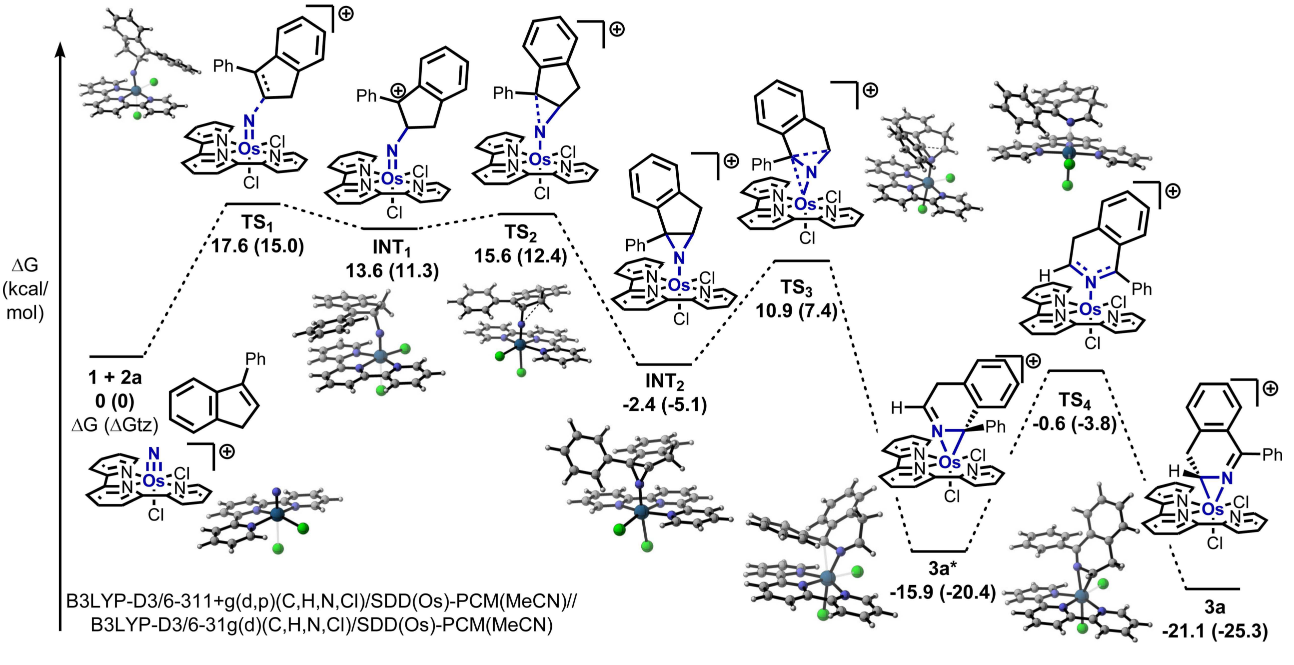

Figure 3. Computational study of the nitrogen insertion reaction mechanism.

suggest that the reaction of the analogous ruthenium(VI) nitride is also feasible through the same pathway (See Supporting Information for details). However, the ruthenium analog of **1** has not been reported and our preliminary attempts towards its preparation were unsuccessful.

Release of the isoquinoline from osmium can be induced by heating **3a** with triethylamine (Et_3N) in MeCN, affording 1-phenylisoquinoline (**4**) and the neutral osmium(II) acetonitrile complex **5**, each in 60 % yield, along with a 35 % yield of **7** (the cationic product observed upon crystallization of **3a**, Figure 4A). The structure of **5** was confirmed by independent synthesis from the reaction of [*trans*-terpyOsNCl$_2$]PF$_6$ with NBu$_4$N$_3$.[50] Treatment of **3a** with trialkylamine[51] at room temperature instead results in the rapid formation of (terpy)Os(1-phenylisoquinoline)Cl$_2$ (**9**), which was isolated in 79 % yield and characterized crystallographically. These observations, coupled with the above kinetic data, in turn raise the question of whether an azaallyl chloride analogous to **8** is an intermediate for the formation of **5**, **7**, and/or **9** (See Figure S2).

Addition of 2 equivalents of exogenous tetrabutylammonium chloride (NBu$_4$Cl) to the base-mediated thermolysis of **3a** did not significantly alter the ratio of **5** and **7**. Additionally, no **9** is observed upon refluxing **7** with NBu$_4$Cl. Together, these observations suggest that chloride dissociation is irreversible. Given the maintenance of both chloride ligands in **9**, an azaallyl chloride intermediate can only be accommodated in its formation if either (i) it forms without association of an acetonitrile ligand, or (ii) internal return of the chloride from the azaallyl fragment is more effective at displacement of acetonitrile than exogenous chloride.

Heating **9** in MeCN results in a 76 % yield of isoquinoline **4** along with an 16 % yield of **7** and an 80 % yield of **5**. Addition of Et_3N and NH_4PF_6 (to mimic the conditions in the thermolysis of **3a**) does not affect this observed ratio of products. Because this distribution diverges meaningfully from the product ratio observed in the reaction of **3a**, it is likely that **3a** does not evolve exclusively through the formation of **9** when heated in the presence of triethylamine. While we cannot therefore rule out the azaallyl chloride as relevant, the balance of evidence suggests it is not an obligate intermediate in the aromatization process.

Completion of a full synthetic cycle from the osmium(II) dichloride **5** was completed via a multi-step oxidative cleavage of the coordinated acetonitrile. Inspired by Meyer's reports of electrochemical oxidation of osmium-ammine complexes, we examined the reaction of **5** with a variety of oxidants and ammonia sources.[52,53] Surprisingly, the use of PhI(OAc)$_2$ and ammonium carbamate or ammonium acetate afforded instead the osmium(III) acetamidine product (**6**, Figure 4B). Oxidation of **5** with an excess of PhI(OAc)$_2$ in the absence of ammonium sources results in the predominant formation of dichloro(terpy)osmium(III) monoacetonitrile. While unexpected, the observation of **6** inspired us to consider nitride generation via C≡N bond cleavage of the acetonitrile ligand.[54] Accordingly, oxidation of **6** in the

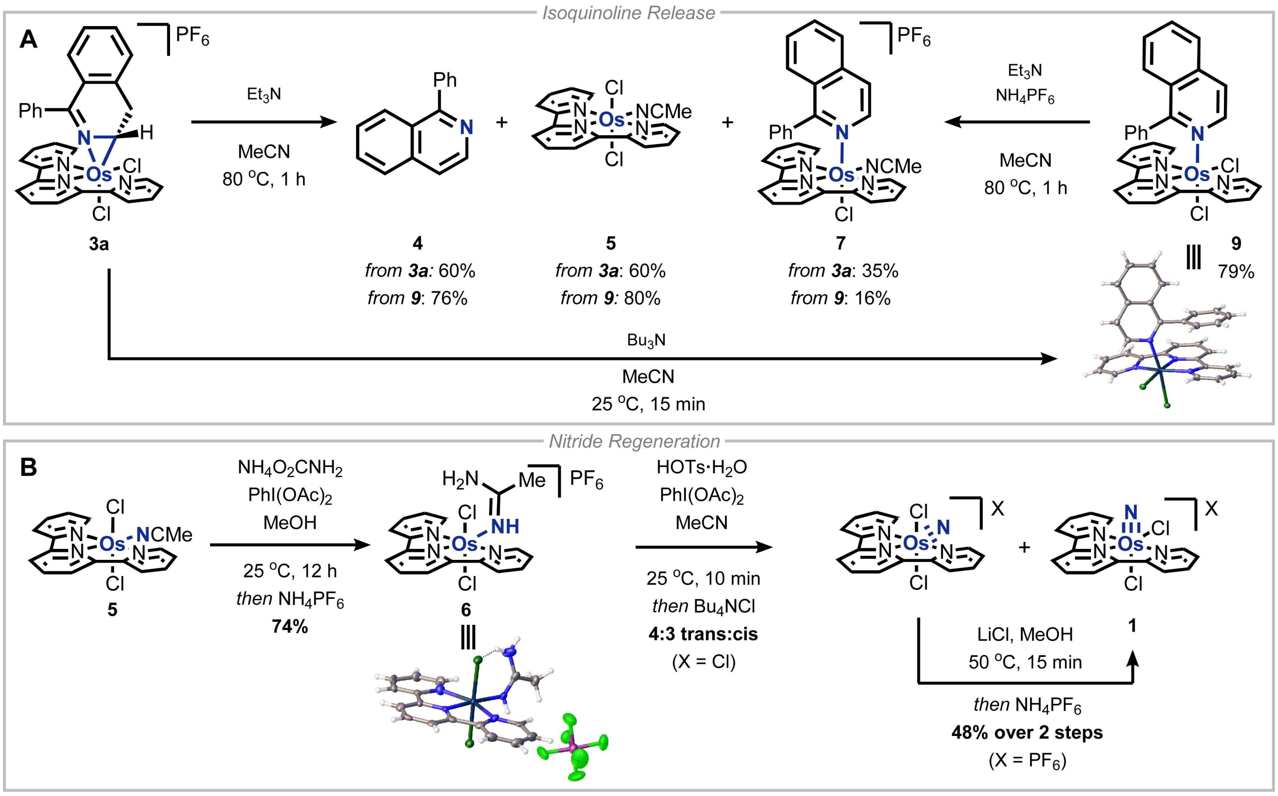

Figure 4. a) Release of isoquinoline facilitated by base, evidence for direct deprotonation of **3**. b) Oxidation and regeneration of the nitride through stepwise cleavage of coordinated acetonitrile.

presence of p-toluenesulfonic acid gives a 4:3 mixture of cis- and trans-nitrides, isolated as chloride salts. This initially gives the trans-osmium(VI) nitride, which is observed in 75 % NMR yield after 5 minutes. Trans-cis isomerization of the osmium(VI) nitride is well precedented, and can be driven to completion by heating in MeOH with an excess of lithium chloride, regenerating **1** to complete the synthetic cycle.[55] Though a four-electron oxidative N-atom transfer could be envisioned to regenerate **1**, only one such example has been well-characterized.[56]

In conclusion, we have demonstrated a synthetic cycle for the synthesis of isoquinolines from indenes via direct N-atom insertion from an osmium(VI) nitride, which sets the stage for the ultimate development of catalytic processes that follow this template. We have additionally shown that azaallenium formation occurs via an aziridination/ring-opening sequence. Aromatization of this species is dominated by direct base-assisted deprotonation, though solvent-assisted migration of the chloride ligand cannot be ruled out as an additional pathway. Finally, we have demonstrated the stepwise oxidative cleavage of an acetonitrile ligand to regenerate the nitride. The nitrogen insertion is computationally feasible for both osmium(VI) and ruthenium(VI) nitrides, suggesting that both metals hold potential for heteroarene synthesis by nitrogen insertion. The mechanistic studies herein shed light on metal nitride insertion processes and point the way towards catalysis via regeneration of the nitrido-ligand.

Supporting Information

Experimental procedures and characterization data (PDF).[57]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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