Synthetic Methods

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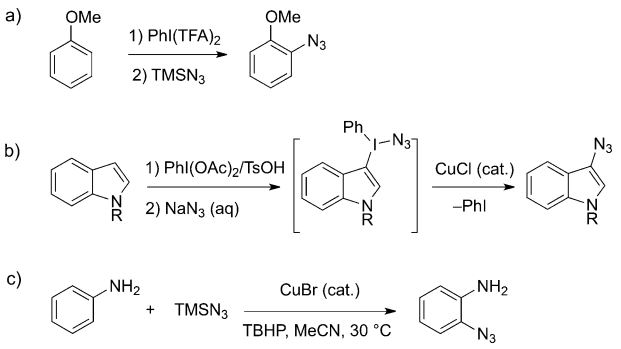
Rhodium(III)-Catalyzed Azidation and Nitration of Arenes by C–H Activation**

*Fang Xie, Zisong Qi, and Xingwei Li**

Organic azide and nitro compounds are important building blocks in synthetic chemistry. In particular, organic azides have found wide applications in synthetic chemistry, material science, polymer chemistry, medicinal chemistry, and biology.[1] Synthetically, azides are particularly well known for copper-catalyzed 1,3-dipolar addition reactions.[2] Furthermore, many azide compounds exhibit valuable biological activities.[3]

Azide groups are introduced by the following methods: 1) the Sandmeyer reaction;[4] 2) the copper-catalyzed coupling of aryl halides or boronic acids with NaN_3 or $TMSN_3$;[5] and 3) the coupling of organometallic reagents with TfN_3.[6] Despite the value of these methods, it is highly attractive to take advantage of the ubiquity of C–H bonds for more step-economical and efficient azidation.[7] To overcome the high strength and low acidity of unreactive C(sp^3)–H bonds, the strategy of homolytic C–H cleavage–azidation has been developed with rather strong hypervalent iodine reagents.[8] Analogously, the same type of hypervalent iodine reagents have been used for the electrophilic azidation of electron-rich arenes, such as anisole and indoles, with and without a metal catalyst (Scheme 1 a,b).[9,10] Significantly, Jiao and Tang developed an elegant system for the copper-catalyzed, NH_2-directed *ortho* C–H azidation of anilines (Scheme 1 c),[11] for which a sequence of single-electron-transfer processes has been proposed.



Scheme 1. C–H azidation of arenes, as described by a) Kita et al.,[9] b) Suna and co-workers,[10] and c) Tang and Jiao.[11] TBHP = *tert*-butyl hydroperoxide, TFA = trifluoroacetate, TMS = trimethylsilyl, Ts = *p*-toluenesulfonyl.

The strategy of transition-metal-catalyzed C–H activation has allowed the development of a plethora of synthetic methods.[12] In particular, C–H activation/coupling reactions catalyzed by stable [Cp^*Rh^{III}] complexes have been explored extensively in the past several years for a broad spectrum of arene substrates bearing a chelating group.[13] However, the coupling partners are mostly limited to π bonds. Rhodium(III)-catalyzed C–H amination has received less attention, and only limited examples of intermolecular C–H amination reactions have been reported, with chloroamines,[14] sulfonyl azides,[15] *N*-fluorobenzenesulfonimide (NFSI),[16] and compounds containing oxidizing N–O bonds[17] as aminating reagents. No C–H azidation of arenes other than electron-rich arenes has been reported, and no related C–H nitration under rhodium catalysis has been documented. We now report a Rh^{III}-catalyzed efficient C–H azidation of arenes bearing chelating groups under relatively mild conditions.

We initiated our studies with the azidation of 2-phenylpyridine with NaN_3. We found that although essentially no C–N coupling occurred when $PhI(OAc)_2$ (PIDA, 1.5 equiv) alone was used as an oxidant in the presence of [{$RhCp^*Cl_2$}$_2$] (4 mol%; Cp^* = pentamethylcyclopentadienyl; Table 1, entry 1), the addition of $TsOH\cdot H_2O$ (1.5 equiv) promoted this coupling in MeCN or CH_2Cl_2 to give the azidation product **2a** in 20–34% yield (entries 2–4). Attempts to improve the catalytic efficiency by employing a cationic rhodium catalyst were to no avail (Table 1, entry 5). We screened a number of solvents and found that the reaction proceeded in CF_3CH_2OH (TFE) in slightly higher yield; however, no reaction occurred in 1,4-dioxane, MeOH, DMF, or $(CF_3)_2CHOH$ (Table 1, entries 6–8). Gratifyingly, **2a** was isolated in high yield when the reaction was conducted in acetone, even under mild conditions (50 °C; Table 1, entry 9). However, lowering of the reaction temperature or the catalyst loading led to a sluggish reaction (Table 1, entries 10 and 11). Impressively, this coupling system proceeded equally well without the extrusion of air or moisture with bench-top acetone, which highlights the operational simplicity of the method (Table 1, entry 13). The reaction also proceeded smoothly when PhI(OTs)OH (Koser reagent, 1.5 equiv) was used in place of PIDA as an oxidant in the presence of AcOH (3 equiv; Table 1, entry 12), which appears to be an active oxidant in the transformation, because it is readily generated from the reaction of PIDA and TsOH.[18] The rhodium catalyst proved necessary: a control experiment showed that essentially no reaction occurred when it was omitted.

[*] Dr. F. Xie,[+] Z. Qi,[+] Prof. Dr. X. Li
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Dalian 116023 (China)
E-mail: xwli@dicp.ac.cn

[+] These authors contributed equally.

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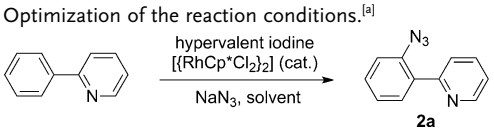
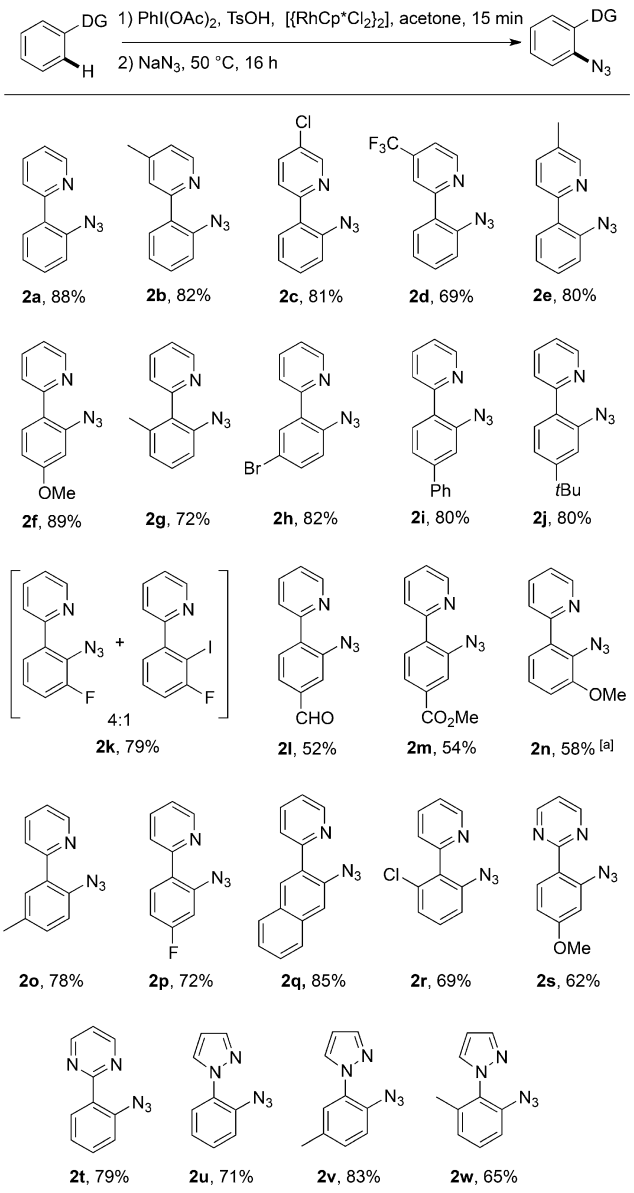
Table 1: Optimization of the reaction conditions.[a]



Entry	Oxidant	Additive	Solvent	*T* [°C]	Yield [%][b]
1	PIDA	–	MeCN	70	< 3
2	PIDA	$TsOH·H_2O$	MeCN	70	20
3	PIDA	$TsOH·H_2O$	MeCN	90	34
4	PIDA	$TsOH·H_2O$	CH_2Cl_2	70	28
5[c]	PIDA	$TsOH·H_2O$	CH_2Cl_2	70	15
6	PIDA	$TsOH·H_2O$	dioxane	90	< 3
7	PIDA	$TsOH·H_2O$	DMF	90	< 3
8	PIDA	$TsOH·H_2O$	TFE	60	40
9	PIDA	$TsOH·H_2O$	acetone	50	88
10	PIDA	$TsOH·H_2O$	acetone	30	68
11[d]	PIDA	$TsOH·H_2O$	acetone	50	56
12	PhI(OH)OTs	AcOH	acetone	50	83
13[e]	PIDA	$TsOH·H_2O$	acetone	50	86

[a] 2-Phenylpyridine (0.3 mmol), the oxidant (0.45 mmol), the acid additive (0.45 mmol for $TsOH·H_2O$ or 0.9 mmol for AcOH), and $[\{RhCp^*Cl_2\}_2]$ (0.012 mmol, 4 mol%) were stirred in the solvent (3 mL) at room temperature for 15 min. NaN_3 (0.9 mmol) was then added, and the mixture was stirred for 16 h at the specified temperature. [b] Yield of the isolated product after chromatography. [c] $AgSbF_6$ (0.048 mmol, 16 mol%) was added. [d] The reaction was performed with 2 mol% of $[\{RhCp^*Cl_2\}_2]$. [e] The reaction was performed without the extrusion of air. DMF = *N*,*N*-dimethylformamide, TFE = CF_3CH_2OH.

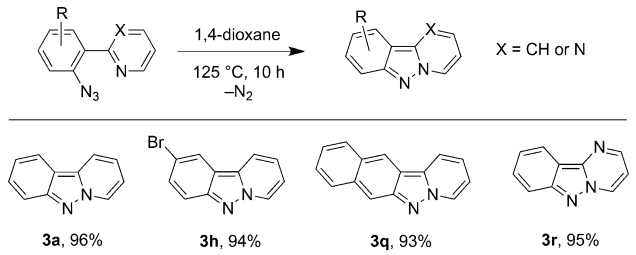


Scheme 2. C–H azidation of arenes. A mixture of the arene (0.3 mmol), PIDA (0.45 mmol), $TsOH·H_2O$ (0.45 mmol), $[\{RhCp^*Cl_2\}_2]$ (4 mol%), and acetone (3 mL) were stirred at room temperature for 15 min, and then NaN_3 (0.9 mmol) was added, and the mixture was stirred at 50°C for 16 h. The yields given are for the isolated products after chromatography. DG = directing group. [a] The other regioisomer was also detected.

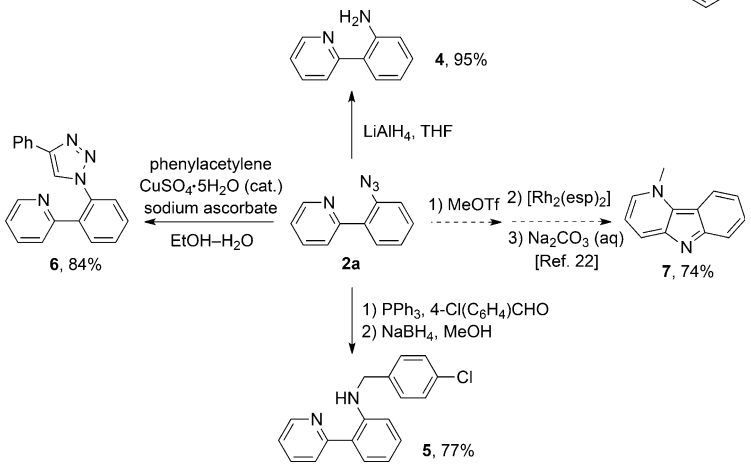
Having optimized the reaction conditions, we next explored the scope and limitations of this reaction (Scheme 2). 2-Phenylpyridines bearing electron-donating, electron-withdrawing, and halogen groups in the pyridine ring were well tolerated, and the azidation products **2a**–**e** were isolated in good to high yield. Similarly smooth coupling was observed for 2-phenylpyridines bearing electron-donating, electron-withdrawing, and halogen groups at different positions of the phenyl ring, although products with electron-withdrawing groups, **2l** and **2m**, were isolated in lower yield. In particular, aldehyde, ester, and bromo groups provide a handle for further functional-group transformations. High regioselectivity for the less hindered *ortho* C–H bond was observed for substrates bearing a *meta* bromo (product **2h**) or methyl group (product **2o**). In contrast, when a smaller but coordinating *meta* fluoro group was introduced, the major product isolated corresponded to azidation at the more hindered *ortho* position (product **2k**), and an iodination product was also obtained with the same regioselectivity. Both regioisomeric azidation products were observed for a *meta*-OMe-substituted substrate, but **2n** was isolated as the major product. This observed regioselectivity for *meta*-F and *meta*-OMe-substituted substrates agrees with that reported for other Rh^{III}-catalyzed C–H activation/coupling reactions.[19] As alternatives to the use of a pyridine directing group, other heterocycles, such as pyrimidines and pyrazoles, are also viable chelating groups; the corresponding azidation products **2t**–**w** were isolated in 65–83% yield. In all cases, no diazidation was observed.

To demonstrate the synthetic usefulness of this method, we derivatized the aryl azide products in several different reactions (Schemes 3 and 4). Denitrogenative N–N coupling was possible even without a catalyst. Thus, when a solution of **2a** in 1,4-dioxane was heated at 125°C, pyrido[1,2-*b*]indazole (**3a**) was formed nearly quantitatively (Scheme 3). Compound **3a** was synthesized previously, but by functionalization of a C–I rather than a C–H bond of a 2-aryl pyridine.[20] Other fused indazole analogues were also obtained in consistently high yields, including from a pyrimidine-functionalized azide substrate (product **3r**).

The synthetic usefulness of the azidation product was further demonstrated by three additional transformations (Scheme 4). Thus, the treatment of **2a** with $LiAlH_4$ gave



Scheme 3. Uncatalyzed denitrogenative C–N coupling.

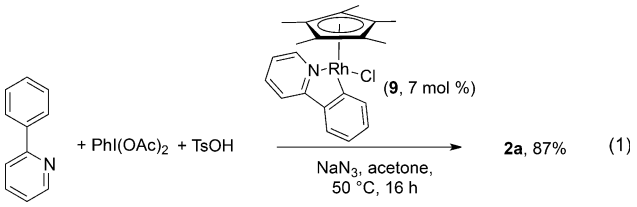


Scheme 4. Functionalization of an aryl azide. esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionate, Tf = trifluoromethanesulfonyl.

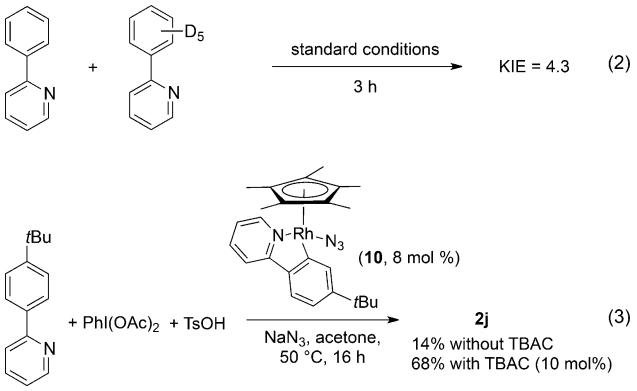
amine **4** in high yield. An aza-Wittig reaction–reduction sequence was used to transform **2a** into the secondary benzylamine **5**. A click reaction of **2a** and PhC≡CH afforded triazole **6** (84%), which could act as a precursor to an abnormal N-heterocyclic carbene ligand.[21] Importantly, Driver and co-workers recently reported that methylation of the pyridine ring of **2a**, followed by $[Rh_2(esp)_2]$-catalyzed nitrene C–H insertion and base treatment, gave carboline **7** in 74% overall yield.[22]

Regioselective nitration is a long-standing challenge.[23] We further expanded our oxidative conditions to arene C–H nitration with $NaNO_2$ as a readily available nitro source. Thus, under slightly modified conditions with the Koser reagent, arenes, including heteroarenes (products **8v–x**), underwent smooth nitration in 40–88% yield (Scheme 5). The scope and regioselectivity of the nitration reaction are similar to those of the azidation. Pyridine, pyrazole, and pyrimidine rings were found to be effective directing groups, and different electron-donating and electron-withdrawing groups in the arene substrates were well tolerated. In particular, pendent formyl, ester, and halogen groups should enable further functionalization. The C–H nitration of arenes under palladium and copper catalysis with chelation assistance has been described previously;[24] however, these systems required harsh conditions (130 °C) and a more expensive stoichiometric $AgNO_3$ or $AgNO_2$ reagent.[24a,b]

We performed several experiments to probe the mechanism of C–H azidation. To explore the relevancy of C–H bond activation, we used a cyclometalated rhodium(III) chloride complex, **9**, as a catalyst (7 mol%) for the azidation of 2-phenylpyridine under otherwise identical conditions. Product **2a** was obtained in essentially the same yield [Eq. (1)], which suggests that this rhodium chloride is

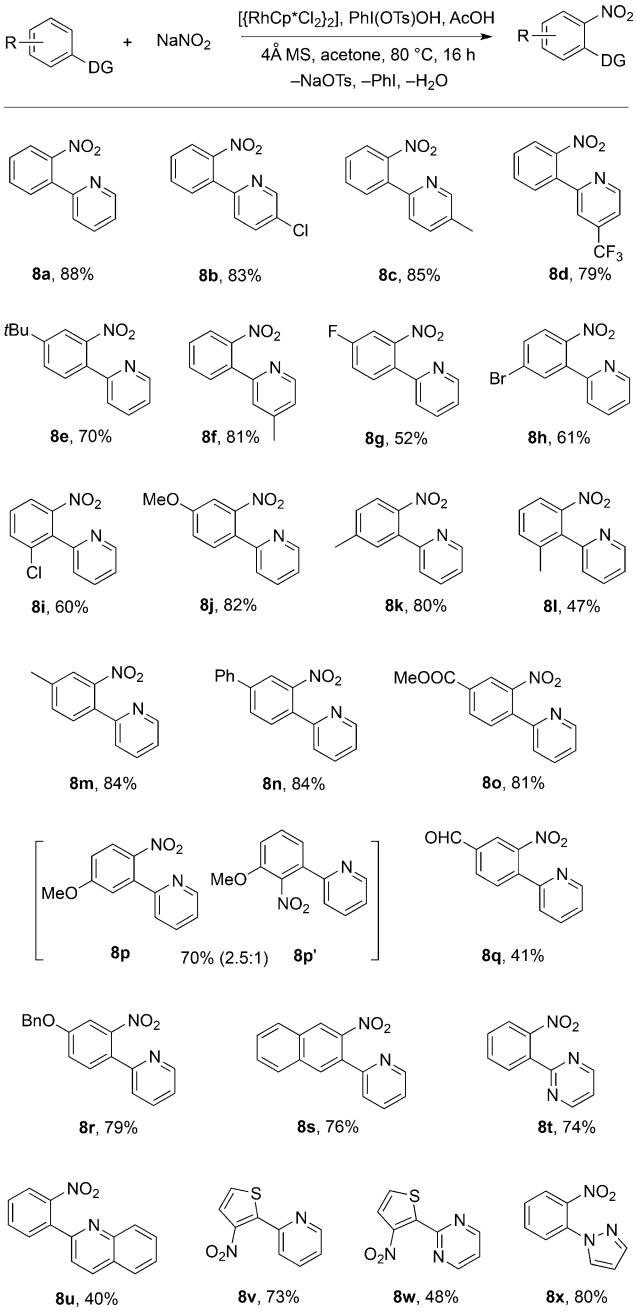


probably a real intermediate. To gain further insight, we measured the kinetic isotope effect (KIE) in the competitive azidation of 2-phenylpyridine and 2-phenyl[D_5]pyridine at low conversion. ^{1}H NMR spectroscopic analysis of the product mixture gave $k_H/k_D = 4.3$ [Eq. (2)]. This large value suggests that the C–H bond cleavage is involved in the rate-limiting step. To assess the possible intermediacy of a rhodium(III) azide, we carried out a reaction with complex **10** (8 mol%) under the standard conditions [Eq. (3)]. Surprisingly, only low conversion into **2j** (14% yield) was observed, which indicated that **10** is not an active catalyst. However, when tetrabutylammonium chloride (TBAC) was used as an additive (10 mol%) with this catalytic system, the



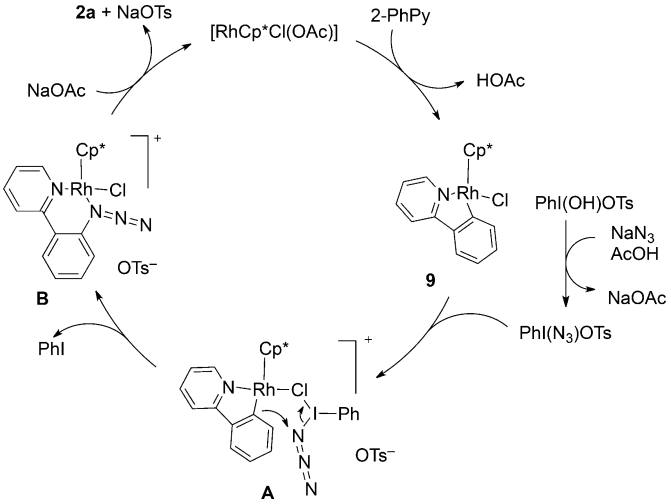
yield of **2j** was improved to 68%. We also found that the cyclometalated Rh^{III} tosylate complex was not an active catalyst (see the Supporting Information). These data seem to suggest that a rhodium chloride intermediate is necessary for efficient catalysis. To probe the intermediacy of organic radical species in the catalysis, we tested 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO; 1 equiv) as an additive for the coupling of 2-phenylpyridine. However, the yield of **2a** (80%) was only slightly affected, which indicated that organic radical species are probably not relevant. Consequently, a mechanism featuring the single-electron oxidation[25] of Rh^{III} species to Rh^{IV} by a hypervalent iodine species is less likely.

On the basis of these observations and literature precedent, we propose a plausible catalytic cycle involving only Rh^{III} species (Scheme 6):[26] The cyclometalation of 2-phenyl-



Scheme 5. Scope of the C–H nitration reaction under similar conditions to those used for azidation (see the Supporting Information for details). Bn = benzyl, MS = molecular sieves.

pyridine (2-PhPy) with an initial [RhCp*(OAc)Cl] catalyst affords a rhodium(III) chloride intermediate **9**, which interacts with the proposed active azidation agent $PhI(N_3)(OTs)$ to give intermediate **A** with a bridging chloride ligand between the metal center and the trivalent iodine atom. Subsequent electrophilic azidation[14,17] via a five-membered-ring transition state is proposed to lead to a rhodacycle **B** and the elimination of PhI. The N,N chelation in intermediate **B** may account for the high selectivity of this reaction for monoazidation. Subsequent release of the coupled product and acetate coordination regenerate the active catalyst.



Scheme 6. Possible catalytic cycle.

In summary, we have reported the first rhodium(III)-catalyzed C–H azidation and nitration reactions of arenes.[27] Sodium azide and sodium nitrite served as readily available nitrogen sources in these reactions, and a common hypervalent iodine reagent was identified as an efficient oxidant. Pyridine, pyrimidine, and pyrazole heterocycles are efficient directing groups. These two systems complement current C–H azidation and nitration reactions. The synthetic utility of the azidation products was demonstrated in subsequent functional-group transformations. Our preliminary mechanistic studies of the azidation reaction suggested that the C–H activation process is involved in the rate-limiting step, and that a cyclometalated Rh^{III} chloride complex is a likely reaction intermediate, whereas a cyclometalated Rh^{III} azide complex is not. Future studies will be directed toward the elucidation of the detailed reaction mechanism.

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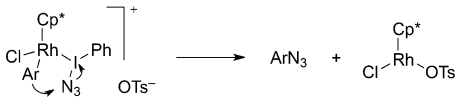
[25] For an elegant example of the single-electron oxidation of Rh^{III} and subsequent reductive elimination of the Rh^{IV} species, see: L. Li, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 12414.

[26] A Rh^{III}–Rh^{I}–Rh^{III} mechanism is unlikely because essentially no reaction occurred when a solution of **9** was heated ([D_6]acetone, 100 °C). However, at this stage we cannot rule out an electrophilic azidation mechanism, in which the iodine in $PhI(N_3)OTs$ may act as a zero-electron ligand. In either mechanism, the role of a chloride ligand is important. Detailed mechanistic studies are under way.



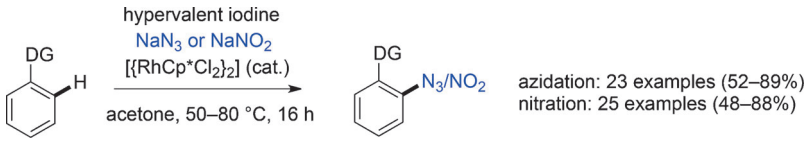
[27] During the final revision of this manuscript, a palladium-catalyzed version of the azidation–cyclization of 2-phenylpyridines to access products **3** was reported in which the azidation product was established as an intermediate: Q.-Z. Zheng, P. Feng, Y.-F. Liang, N. Jiao, *Org. Lett.* **2013**, *15*, 4262.

Communications

Synthetic Methods

F. Xie, Z. Qi, X. Li* _____ ■■■■–■■■■

Rhodium(III)-Catalyzed Azidation and Nitration of Arenes by C–H Activation



Getting a handle on it: In the chelation-assisted title reactions in the presence of a hypervalent iodine oxidant, sodium azide and sodium nitrite served as readily available nitrogen sources, and pyridine, pyrimidine, and pyrazole substituents were efficient directing groups (DGs; see scheme; $Cp^* = C_5Me_5$). The synthetic utility of the azidation products was demonstrated in subsequent functional-group transformations.

