Catalytic Amination

DOI: 10.1002/ange.201302784

Direct C–H Amination of Arenes with Alkyl Azides under Rhodium Catalysis**

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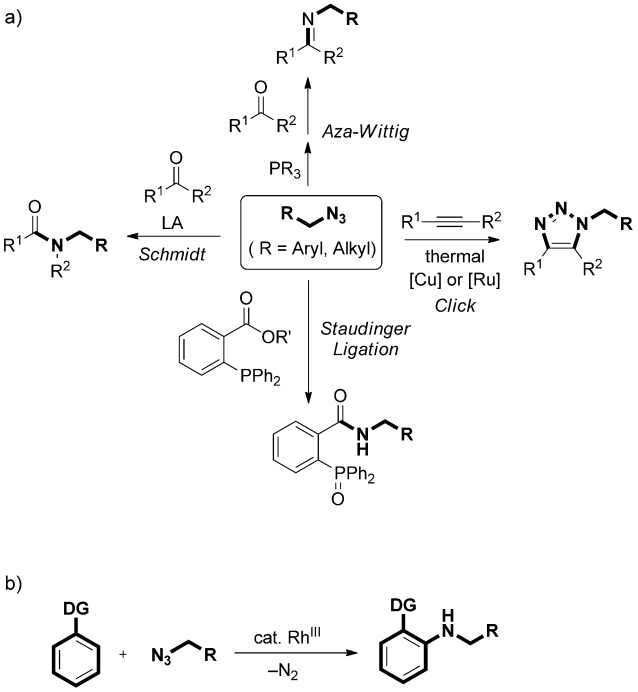
Dedicated to Professor Chul-Ho Jun on the occasion of his 60th birthday

Since the seminal study by Curtius on the use of alkyl azides in organic chemistry, particularly in C–N bond-forming reactions, these readily available compounds have been widely used as one of the most convenient amino sources.[1] The four most notable examples of such reactions are the Schmidt rearrangement,[2] the aza-Wittig reaction,[3] cycloaddition with alkynes,[4] and the Staudinger ligation[5] (Scheme 1). Whereas an amide bond is readily generated in the Schmidt reaction, imine formation is facile under the aza-Wittig conditions. The copper-mediated reaction of alkyl azides with 1-alkynes has been well developed as a connecting tool in various fields of research. Furthermore, alkyl azides are a key component of the Staudinger ligation for the formation of amides even in vivo.[6]

Despite the significant advances made in the use of alkyl azides as the nitrogen source for C–N bond formation, the use of these widely available compounds in metal-mediated direct C–H amination has rarely been investigated.[7–9] Although N-alkylimido (nitrenoid) metal complexes are known to be generated,[10] the alkyl groups used are very limited even with specially designed ligand systems. Moreover, only a few examples of C–N bond formation upon treatment of the corresponding N-alkylimido metal species with hydrocarbons have been reported.[10e,f,h] When compared to the Buchwald–Hartwig amination procedure, in which (hetero)aryl halides are treated with amines,[11] the direct C–H amination of (hetero)arenes displays notable advantages as a more straightforward route to C–N bond formation. As a result, extensive studies on direct C–H amination have been carried out, mainly with palladium[12] and copper catalysts.[13] However, amino sources are limited largely to amides, although reaction conditions have been improved to enable the use of a broader range of substrates. Direct C–H amination with *N*-hydroxy-[14] and *N*-chloroamines has also been investigated,[13e,15] but its scope is still limited to the use of secondary amine precursors to afford tertiary amine products.



Scheme 1. a) Previously developed C–N bond-forming reactions with alkyl azides. b) The reaction developed in this study: a rhodium-catalyzed direct C–H amination with alkyl azides. DG = directing group, LA = Lewis acid.

During our continuing efforts to develop the direct introduction of amino groups into (hetero)arenes with high synthetic utility,[16] we recently reported rhodium-catalyzed C–H amination procedures with sulfonyl and aryl azides as unique amino sources.[17,18] The reactions proceed without an external oxidant to release molecular nitrogen as the only by-product. Although they feature broad substrate generality with high functional-group tolerance, the installation of an alkylamino group was also envisioned to be highly desirable, as synthetically more important and diverse N-alkylaniline products could be accessed directly by such an approach. Furthermore, owing to the development of click cycloaddition chemistry,[4] a wide range of alkyl azides are available, including biologically relevant compounds, such as sugars and peptides. In this context, we report herein the first rhodium-catalyzed direct C–H amination of arenes with alkyl azides.

We first sought an optimal catalytic system for the direct amination of arene C–H bonds with a series of benzyl and

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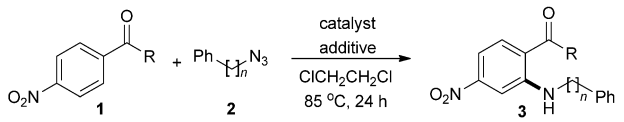
[**] This research was supported financially by the Institute of Basic Science (IBS).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302784.

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

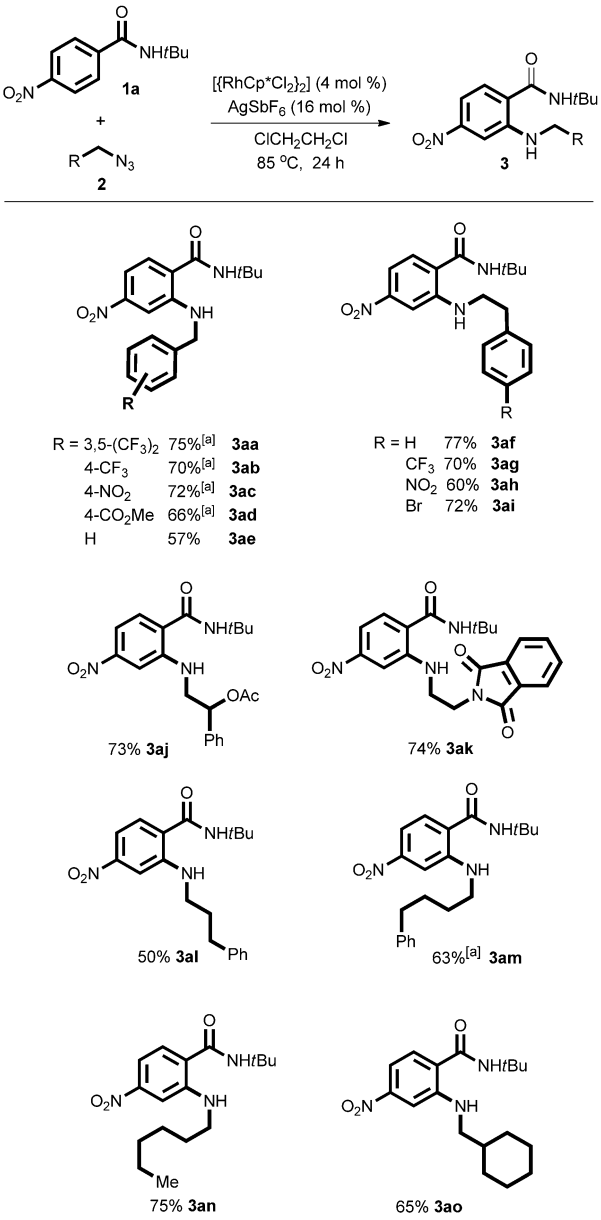


Entry	R	*n*	Catalyst (mol%)	Yield[b]
1	NH_2	1	$[\{RhCp^*Cl_2\}_2]$ (4)/$AgSbF_6$ (16)	11
2	NMe_2	1	$[\{RhCp^*Cl_2\}_2]$ (4)/$AgSbF_6$ (16)	N.R.
3	OEt	1	$[\{RhCp^*Cl_2\}_2]$ (4)/$AgSbF_6$ (16)	N.R.
4	NHMe	1	$[\{RhCp^*Cl_2\}_2]$ (4)/$AgSbF_6$ (16)	15
5	NH*t*Bu	1	$[\{RhCp^*Cl_2\}_2]$ (4)/$AgSbF_6$ (16)	**65 (57)**
6[c]	NH*t*Bu	1	$Pd(OTf)_2$ (10)	N.R.
7	NH*t*Bu	1	$[PdCl_2(MeCN)_2]$ (10)	N.R.
8	NH*t*Bu	1	$[Rh_2(O_2CCF_3)_4]$ (4)	N.R.
9[d]	NH*t*Bu	1	$[Rh_2(O_2CCF_3)_4]$ (4)	N.R.
10	NH*t*Bu	1	$[\{Ru(p\text{-cymene})Cl_2\}_2]$ (4)/AgSbF6 (16)	< 5
11	NH*t*Bu	2	$[\{RhCp^*Cl_2\}_2]$ (4)/$AgSbF_6$ (16)	**85 (77)**
12	NH*t*Bu	3	$[\{RhCp^*Cl_2\}_2]$ (4)/$AgSbF_6$ (16)	50
13	NH*t*Bu	4	$[\{RhCp^*Cl_2\}_2]$ (4)/$AgSbF_6$ (16)	45

[a] Reaction conditions: **1** (0.36 mmol), **2** (0.2 mmol), 1,2-dichloroethane (0.5 mL). [b] The yield was determined by ^1H NMR spectroscopy. Where applicable, the yield of the isolated product is given in parentheses. [c] $Na_2S_2O_8$ (1 equiv) and HOTf (0.5 equiv) were added. [d] $PhI(OAc)_2$ (1 equiv) was added. Cp* = pentamethylcyclopentadienyl, N.R. = no reaction, Tf = trifluoromethanesulfonyl.

alkyl azides (Table 1). With a cationic Rh^{III} catalyst generated in situ from $[\{RhCp^*Cl_2\}_2]$ and a silver additive,[19] no significant conversion was observed when primary or tertiary benzamides were treated with benzyl azide ($n = 1$; Table 1, entries 1 and 2).[20] An ester was not an effective directing group (Table 1, entry 3). In contrast, secondary *N*-alkyl benzamides were aminated in varying yields, depending on the *N*-alkyl group. For example, whereas the amination of *N*-methylbenzamide was sluggish and gave the desired product in low yield (Table 1, entry 4), *N-tert*-butylbenzamide underwent more efficient amination with benzyl azide (Table 1, entry 5). Other catalytic systems known to facilitate previously described amination or amidation reactions based on a nitrenoid-insertion pathway[12b,g] were found to be ineffective (Table 1, entries 6–10). Not only benzyl azide but also alkyl azides ($n = 2$ or higher) functioned as an effective amino source in the rhodium-catalyzed reaction (Table 1, entries 11–13).

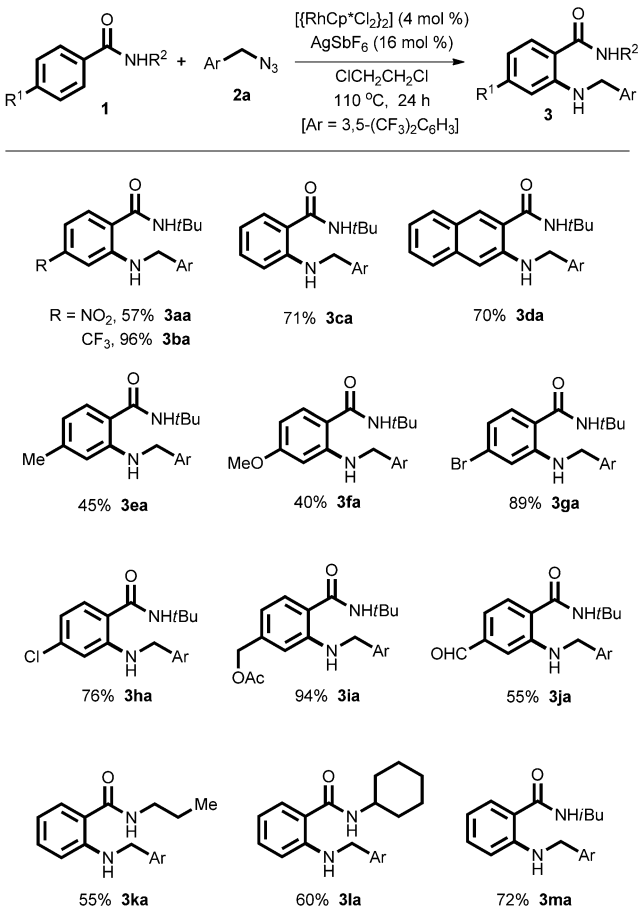
On the basis of these promising results, we further investigated the scope of the direct C–H amination of alkyl azides with *N-tert*-butyl-4-nitrobenzamide (**1a**) as a standard substrate (Scheme 2). Although the amination took place smoothly in general, benzyl azides bearing electron-withdrawing substituents afforded the corresponding products **3aa**–**3ad** in slightly higher yields. An excess of the azide was used in these cases (2 equiv with respect to **1**); thus, the procedure is flexible and can be adjusted readily for the amination of more precious substrates. As anticipated, the electronic influence was alleviated when phenethyl azides were used (products **3af**–**3ai**). Alkyl azides bearing acetyl and phthalimido groups underwent the amination in good yield to give **3aj** and **3ak**, respectively. We were pleased to observe



Scheme 2. Scope of the reaction with respect to the alkyl azide substrate: **1a** (0.36 mmol), **2** (0.2 mmol), 1,2-dichloroethane (1,2-DCE; 0.5 mL). In each case, the yield of the isolated product is given. [a] The reaction was carried out with **1a** and **2** in a 1:2 ratio at 110 °C for 24 h.

that aliphatic azides also participated in the reaction with similar efficiency (products **3an** and **3ao**).

The range of possible benzamide substrates was then studied in the reaction with 3,5-bis(trifluoromethyl)benzyl azide (**2a**; 2 equiv; Scheme 3). The reaction proceeded smoothly to afford *ortho*-aminated products in moderate to good yields, although the use of benzamides bearing electron-donating groups led to decreased yields (e.g. in the synthesis of **3ea** and **3fa**). 2-Naphthamide was aminated at the less hindered position to give **3da** in good yield. Various functional groups commonly encountered in organic synthesis were tolerated well, such as halide (products **3ga**, **3ha**), acetate (product **3ia**), and aldehyde groups (product **3ja**).



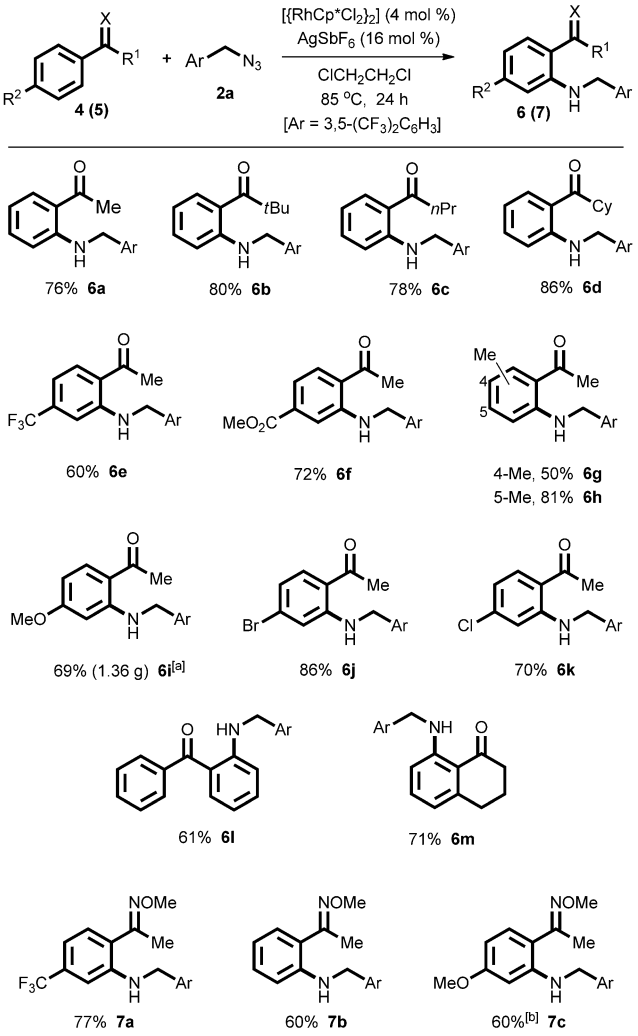
Scheme 3. Scope of the reaction with respect to the benzamide substrate: **1** (0.2 mmol), **2a** (0.4 mmol), 1,2-DCE (0.5 mL). In each case, the yield of the isolated product is given.

Notably, the amination was efficient regardless of the *N*-alkyl moiety of the secondary benzamide (products **3ka**–**3ma**).

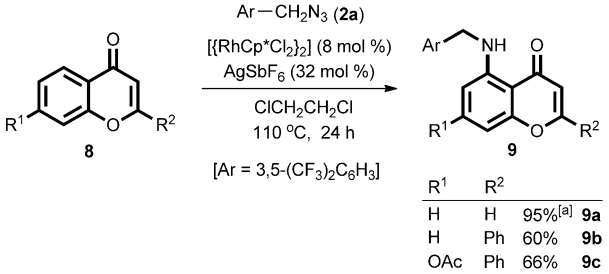
Encouraged by these results, we turned our attention to additional substrates bearing weak coordinating groups. To our delight, we observed that aromatic ketones were readily aminated to afford synthetically useful *ortho*-aminoaryl ketones (Scheme 4).[21] Aryl alkyl ketones bearing primary, secondary, and tertiary alkyl moieties all underwent the amination in satisfactory yields (products **6a**–**6d**). These results suggest that the present reaction is not influenced by the steric bulk of the substrates. Unlike in the benzamide substrates (Scheme 3), electronic variation of the aromatic substituent in the aryl ketones had little effect on the reaction efficiency (products **6e**–**6k**). The amination reaction could be scaled up without difficulty, as demonstrated in the production of **6i**. Benzophenone and 1-tetralone were also smoothly aminated to give **6l** and **6m**, respectively. Aryl ketoximes were also good substrates for this amination under similar conditions, irrespective of the electronic nature of substituents on the aromatic ring (products **7a**–**7c**).

We were pleased to find that chromone and flavones were also aminated in synthetically acceptable yields (Scheme 5). Since 5′-aminochromones and their flavone derivatives are known to exhibit interesting biological activity,[22] our method shows high value, as it offers the most straightforward route to these compounds.

One of the most striking features of the use of alkyl azides lies in the ready access to structurally diverse compounds,

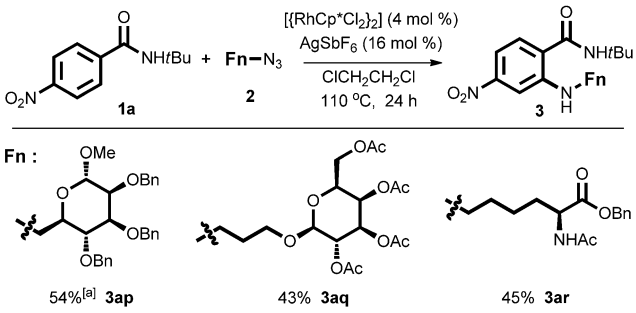


Scheme 4. Scope of the reaction for the amination of aryl ketones and ketoximes: **4** or **5** (0.2 mmol), **2a** (0.4 mmol), 1,2-DCE (0.5 mL). In each case, the yield of the isolated product is given. [a] The reaction was carried out on a 5 mmol scale (with 5 mmol of 4-methoxyacetophenone). [b] The reaction was carried out at 110 °C. Cy = cyclohexyl.

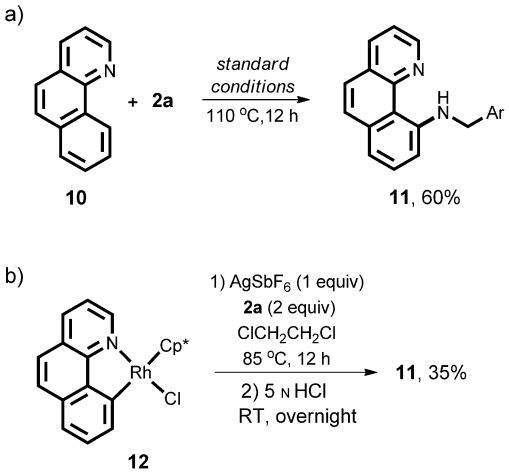


R^1	R^2		
H	H	95%[a]	**9a**
H	Ph	60%	**9b**
OAc	Ph	66%	**9c**

Scheme 5. Direct C—H amination of chromone and flavones: **8** (0.2 mmol), **2a** (0.4 mmol), 1,2-DCE (0.5 mL). In each case, the yield of the isolated product is given. [a] The reaction was carried out with 4 mol% of the Rh catalyst and 16 mol% of the Ag additive.



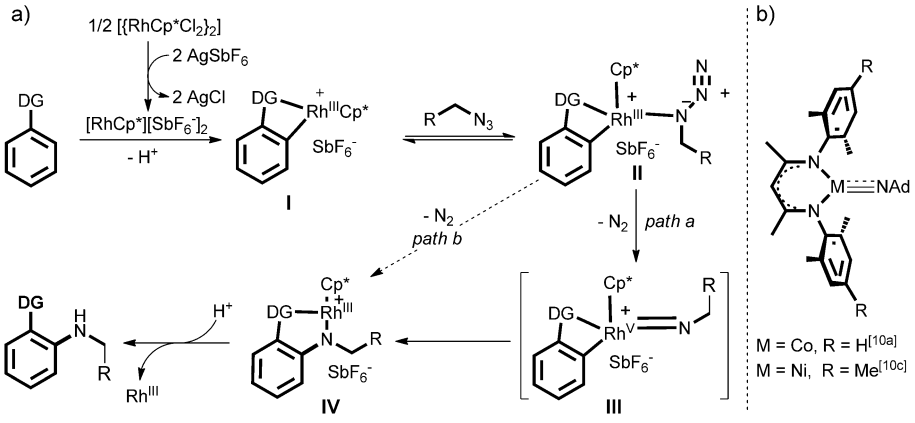
Scheme 6. Application of biologically relevant alkyl azides: **1a** (0.2 mmol), **2** (0.4 mmol), 1,2-DCE (0.5 mL). In each case, the yield of the isolated product is given. [a] The reaction was carried out at 85 °C. Bn = benzyl.



Scheme 7. a) Catalytic amination of benzo[*h*]quinoline (**10**). b) Stoichiometric reaction with the cyclometalated rhodium complex **12**. Ar = 3,5-$(CF_3)_2C_6H_3$.

mainly as a result of the remarkable advances that have been made in click chemistry.[4] We successfully applied our protocol to the introduction of biologically relevant sugar and amino acid groups by using the corresponding alkyl azides (Scheme 6).

To shed light on the reaction mechanism of this amination reaction, we conducted isotope labeling experiments with deuterium-labeled benzamides.[23] Significant primary kinetic isotope effects were observed on the basis of an intermolecular competition experiment in one vessel ($P_H/P_D = 4.0$) and in a parallel experiment ($k_H/k_D = 1.7$). Moreover, no H/D scrambling was found to occur between substrates. These results suggest that the C–H bond cleavage of arenes is irreversible and rate-limiting with the present rhodium catalyst system.



Scheme 8. a) Proposed mechanism of the direct C–H amination. b) Examples of isolated metal alkylimido complexes. Ad = adamantyl.

Benzo[*h*]quinoline (**10**) was aminated readily under the standard conditions to give **11** (Scheme 7a), and the treatment of a pregenerated cyclometalated rhodium complex **12**[24] with azide **2a** also gave the aminated product **11**, albeit in moderate yield (Scheme 7b). Importantly, in a separate experiment, **12** catalyzed the amination of **10** in 70% yield;[23] thus, the intermediacy of a cyclometalated rhodium complex in the catalytic cycle is plausible.

A plausible amination pathway based on these mechanistic studies as well as previously reported studies[25–27] is depicted in Scheme 8a. First, irreversible C–H bond cleavage by a cationic rhodium species leads to the formation of a five-membered rhodacyclic intermediate **I**. Coordination of the alkyl azide to **I** would form an intermediate **II**, and subsequent insertion of the *N*-alkylamido group into the rhodacycle would afford a Rh^{III} amido species **IV**. In this process, either a stepwise nitrenoid pathway (path a) or concerted migratory insertion route (path b) would be possible. Finally, protonolysis of complex **IV** would deliver the *N*-alkylaniline product. In fact, a range of metal alkyl nitrenoids are known to be generated in reactions of alkyl azides with Co,[10a,b,d] Ni,[10c,g,i] Cu,[10e] and Fe complexes,[10f,h] and some of those species were indeed isolated (Scheme 8b).[10a–d] In this context, we postulate that alkyl azides react with the rhodacycle to furnish the corresponding nitrenoids, as proposed in our previous studies with sulfonyl and aryl azides.[17]

To further investigate electronic effects on the reaction rates, we also performed intermolecular competition experiments. The observation that amination was faster with both benzamide and acetophenone[23] substrates bearing electron-rich substituents strongly suggests that this amination does not proceed through a nucleophilic aromatic substitution (S_NAr) pathway.[28] Furthermore, a competition experiment between benzyl azide and an aryl azide in a reaction with benzamide showed significantly higher reactivity of benzyl azide over the aryl azide.[23] This result implies that the rate of the final protonolysis step in the catalytic cycle closely reflects the degree of nucleophilicity of the presumed rhodacyclic intermediate **IV** (Scheme 8).

In conclusion, we have developed a straightforward procedure for the insertion of an amino group into arene C–H bonds by the use of alkyl azides as the nitrogen source. Both benzyl and aliphatic azides bearing a wide range of functional groups of high biological interest reacted readily with a range of substrates containing chelating groups under Rh^{III} catalysis. The excellent functional-group tolerance observed will enable this transformation to be applied as a convenient route to synthetically and medicinally important amino compounds.

Experimental Section

Representative procedure: *N-tert*-Butyl-4-nitrobenzamide (**1a**; 80 mg, 0.36 mmol), phenethyl azide (**2f**; 27 μL, 0.2 mmol), [{RhCp*Cl_2}$_2$] (4.9 mg, 4 mol%), $AgSbF_6$ (11.0 mg, 16 mol%), and 1,2-dichloroethane (0.5 mL) were placed in a screw-cap vial equipped with a Spinvane triangular stir bar under atmospheric conditions. The reaction mixture was stirred in a preheated oil bath at 85 °C for 24 h, cooled to room temperature, filtered through a pad of Celite, and then washed with CH_2Cl_2 (3 × 10 mL). Organic solvents were removed under reduced pressure, and the residue was purified by silica-gel chromatography (*n*-hexane/EtOAc, 10:1, v/v) to give **3af** (52.6 mg, 77%).

Received: April 4, 2013
Revised: May 20, 2013
Published online: June 20, 2013

Keywords: alkyl nitrenoids · aniline derivatives · azides · C–H amination · rhodium catalysis

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