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C–H Activation

Rhodium-Catalyzed Direct Amination of Arenes with Nitrosobenzenes: A New Route to Diarylamines

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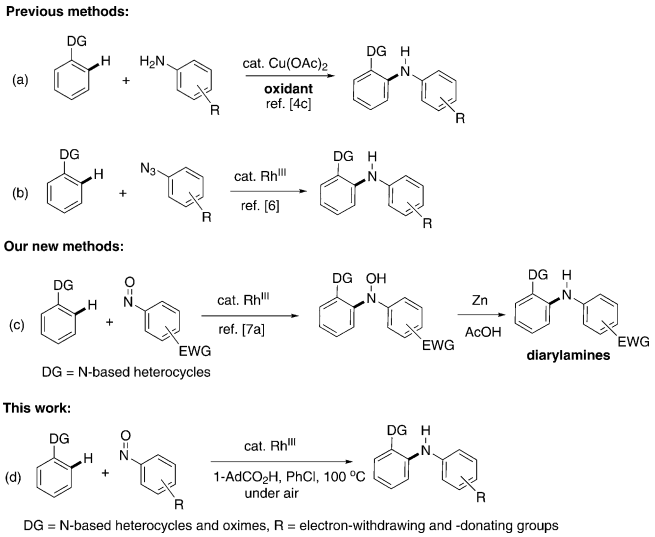
Abstract: A Rh^{III}-catalyzed addition of aryl C–H bonds to nitrosobenzenes, followed by cleavage of the resulting hydroxylamines in situ, has been reported. Different directing groups, such as N-based heterocycles and ketoximes, can be used in this C–H amination process, providing valuable diarylamines in excellent yields. Most importantly, this process provides a new method for attaching arylamine groups to aromatic rings.

Introduction

Diarylamines are ubiquitous structural motifs in numerous biologically active natural products, pharmaceuticals, dyes, agrochemicals, and functional materials.[1] Metal-mediated cross-coupling reactions of aryl (pseudo)halides with anilines has been developed as a powerful tool for the synthesis of diarylamines.[2] However, these methods require time-consuming and tedious prefunctionalization of substrates. With the increasing interest in transition-metal-catalyzed functionalization of C–H bonds, the development of a direct intermolecular amination of arene C–H bonds with anilines is highly desirable.[3]

Recent studies have demonstrated that two strategies have been successfully developed for metal-catalyzed direct C–H amination. The first strategy is to employ parent amines in the presence of external oxidants.[4] An alternative strategy is the use of preactivated amine precursors.[5] However, these reactions are, in most cases, limited to amide or alkylamine coupling partners.[4,5] Only a few examples involving the formation of diarylamines have been reported, with narrow substrate scope and low efficiency (Scheme 1 a).[4c] Moreover, these reactions usually generate stoichiometric by-products from the external oxidants,[4] or halide salts.[5] Recently, a Rh-catalyzed C–H amination of arenes with aromatic azides has been reported to provide diarylamines (Scheme 1 b).[6] Although this approach is highly promising, there is a safety risk in the handling of azides, especially when the reactions are carried out on a large scale. Given the prevalence of diarylamines and the limitation of previous methods,[4c,6] further development of novel catalytic arene C–H amination reactions, to enable the formation of valuable diarylamines (especially diarylamines that can be synthesized from readily available amine sources), would be highly desirable and of prime synthetic value.



Scheme 1. The formation of diarylamines by means of C–H activation.

Recently, we developed a Rh-catalyzed addition of aryl C–H bonds to electron-withdrawing nitrosobenzenes to give *N*,*N*-diaryl hydroxyl amines, which could be reduced in the presence of Zn/AcOH to afford diarylamines (Scheme 1 c).[7a] Very recently, we disclosed a Rh^{III}-catalyzed aryl C–H amidation with *N*-hydroxycarbamates under oxidative conditions, giving access to *N*-carbamate-protected arylamines.[7b] Inspired by these results, and other Rh^{III}-catalyzed aryl C–H bond functionalizations,[8–12] we herein report a Rh-catalyzed aryl C–H addition to nitrosobenzenes, under an air atmosphere, followed by cleavage of the resulting hydroxylamines in situ to produce valuable and versatile diarylamines in excellent yields (Scheme 1 d). Significantly, different directing groups, such as pyridine, pyrimidine, pyrazole, and ketoxime, can be employed in this C–H amination reaction, and various synthetically im-

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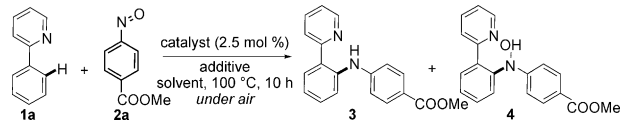
portant functional groups (e.g., halogen, ester, and aldehyde moieties) are tolerated.

Results and Discussion

2-Phenylpyridine (**1a**) and methyl 4-nitrosobenzoate (**2a**) were chosen as the model substrates (Table 1). When **1a** was treated with $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (2.5 mol%, Cp^* = pentamethylcyclopentadienyl and **2a** in PhCl, at 100 °C for 10 h under air, the

Table 1. Optimization of Rh-catalyzed C–H amination reaction.[a]

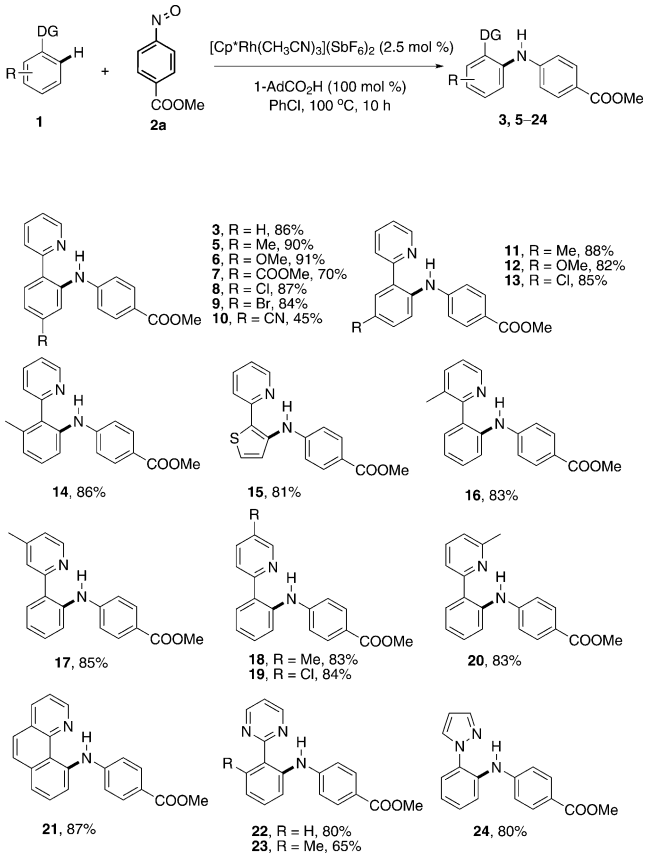


Entry	Catalyst [2.5 mol%]	Additive	Solvent	3 [%]	4 [%]
1	$(Cp^*RhCl_2)_2$	–	PhCl	0	0
2	$(Cp^*RhCl_2)_2/AgSbF_6$	–	PhCl	15	5
3	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	–	PhCl	35	4
4	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Cs_2CO_3	PhCl	0	0
5	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	PivOK	PhCl	0	0
6	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	$Cu(OAc)_2$	PhCl	30	4
7	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AcOH	PhCl	45	0
8	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	PivOH	PhCl	70	3
9	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	1-$AdCO_2H$	PhCl	86	0
10	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	1-$AdCO_2H$	DCE	50	4
11	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	1-$AdCO_2H$	THF	45	4
12	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	1-$AdCO_2H$	CH_3OH	49	5
13	–	1-$AdCO_2H$	PhCl	0	0
14	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	1-$AdCO_2H$ H_2O (5 equiv)	PhCl	85	0

[a] **1a** (0.2 mmol), **2a** (0.24 mmol), catalyst (0.005 mmol), additive (0.2 mmol), and solvent (1 mL) at 100 °C for 10 h. Yield of isolated product. 1-$AdCO_2H$ = 1-Adamantane carboxylic acid; PivOH = pivalic acid; DCE = 1,2-dichloroethane.

desired diarylamine, **3**, was obtained in 35% yield, possibly resulting from cleavage of *N*,*N*-diaryl hydroxylamine **4** (entry 3).[13] The structure of **3** was confirmed by X-ray crystallography (Figure 1).[14] No product was observed with the addition of a base (entries 4 and 5). In contrast, the addition of an acid gave a dramatic increase in the reaction yield (entries 7–9) and 1-$AdCO_2H$ proved to be particularly effective (entry 9). Of the different solvents tested (entries 9–12) PhCl was found to be the best solvent for the reaction (entries 9). Control experiments revealed that the Rh^{III} complex is essential and that the addition of water did not affect the yield (entries 13–14).

With the optimized reaction conditions in hand, the substrate scope, with respect to 2-arylpyridines, was subsequently explored and the results are summarized in Scheme 2. 2-Arylpyridines bearing both electron-donating and electron-withdrawing groups were viable substrates for this amination reaction, giving the corresponding diarylamine products (**5**–**14**) in good to excellent yields. *meta*-Substituted derivatives underwent this amination reaction only at the sterically more accessible C–H bond (**11**–**13**). In particular, the 2-methyl derivative smoothly afforded the corresponding product (**14**) in excellent yield, thus indicating high steric tolerance of this system. Moreover, the tolerance of various functional groups, such as



Scheme 2. Substrate scope. Reaction conditions: $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (2.5 mol%), substrate **1** (0.2 mmol), **2a** (0.24 mmol), 1-$AdCO_2H$ (0.2 mmol), and PhCl (1 mL), for 10 h at 100 °C. Yields of isolated product are shown.

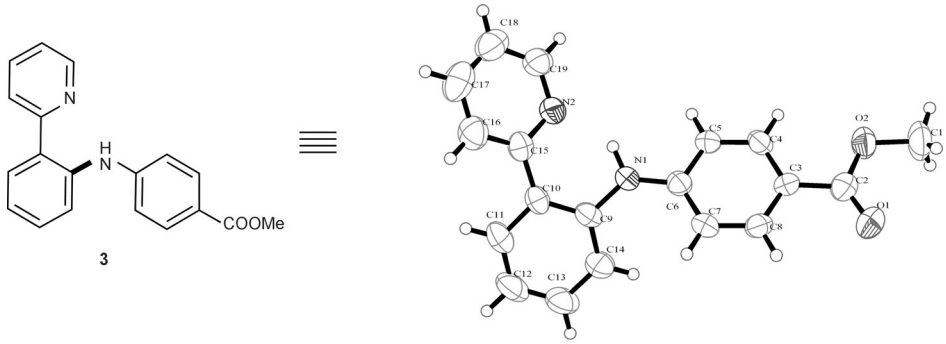
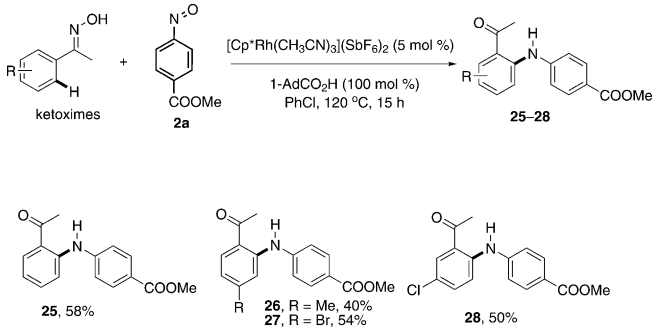


Figure 1. X-ray crystallographic structure of **3**.

ester (**7**), chloro (**8** and **13**), bromo (**9**), and nitrile (**10**) groups, afforded a great opportunity for further functionalization. In addition, we were delighted to find that heterocyclic substrates (**15**) proved to be reactive.

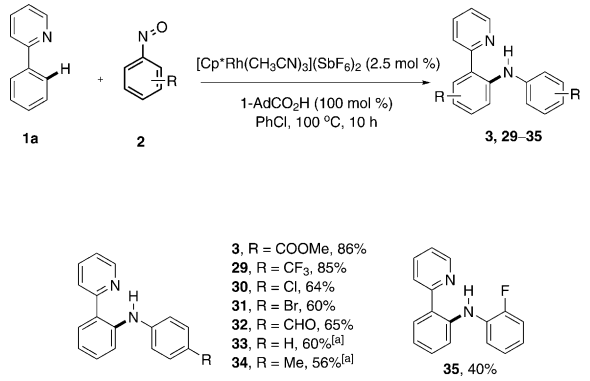
We next evaluated various pyridinyl directing groups. Electron-rich and electron-poor pyridine rings were well tolerated (**16**–**20**) and the influence of the steric bulk on the pyridine ring was minor for this C–H amination reaction (**16**–**18** and **20**). Notably, benzo[*h*]quinolone (**21**) and other heterocycles, such as pyrimidine (**22** and **23**) and pyrazole (**24**), also worked well as effective directing groups.

Notably, in addition to N-based heterocycles, more common and synthetically useful ketoximes also reacted well as a directing group to facilitate the amination reaction (Scheme 3). Interestingly, on using an oxime group as the directing group, an anilino unit was selectively inserted at the *ortho*-position of the oxime group, followed by in situ deprotection to afford 2-anilinoacetophenones (**25**–**28**).



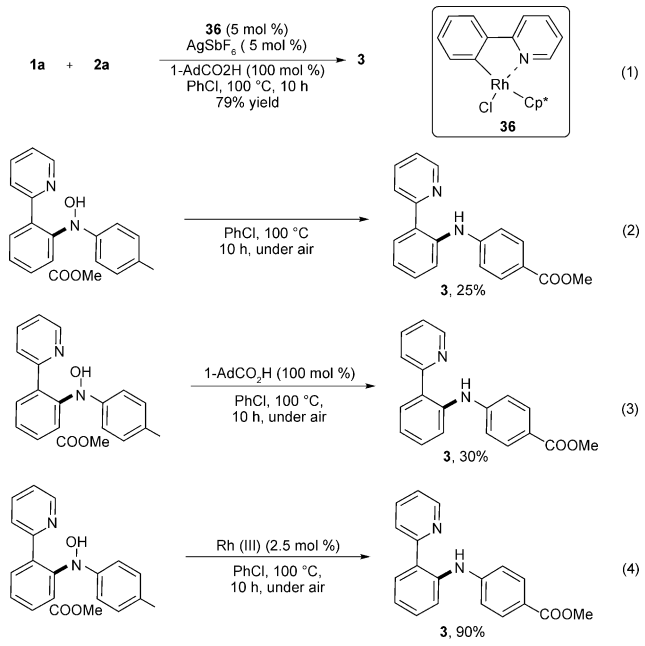
Scheme 3. Ketoxime substrate scope. Reaction conditions: $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (2.5 mol%), ketoxime (0.2 mmol), **2a** (0.24 mmol), 1-$AdCO_2H$ (0.2 mmol), and PhCl (1 mL), for 10 h at 100 °C. Yields of isolated product are shown.

The scope of nitrosobenzenes was then examined (Scheme 4). In particular, not only electron-poor nitrosobenzenes (**29**–**32**), but also electron-neutral (**33**) and even electron-rich (**34**) nitrosobenzenes gave the desired diarylamines in high to excellent yields, emphasizing the generality of this method. In a similar manner to the reactions of 2-arylpyridines, a variety of functional groups (e.g., ester (**3**), halogen (**30**, **31**, and **35**), and even the electrophilic carboxaldehyde (**32**) groups) were compatible with this amination reaction, allowing for high diversity in the synthesis of diarylamines.

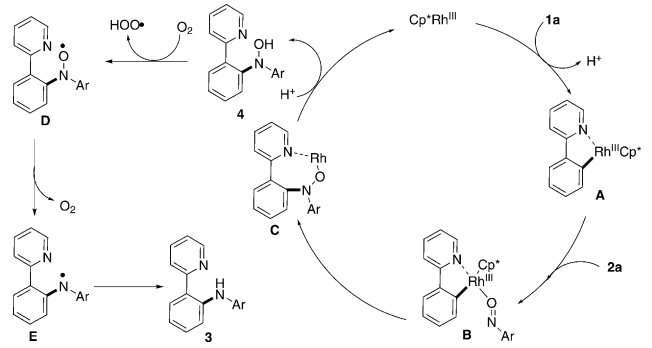


Scheme 4. Nitrosobenzene substrate scope. Reaction conditions: $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (2.5 mol%), substrate **1a** (0.2 mmol), **2** (0.24 mmol), 1-$AdCO_2H$ (0.2 mmol), and PhCl (1 mL), for 10 h at 100 °C. Yields of isolated product are shown. [a] $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (5 mol%) and PhCl (0.4 mL) were used at 130 °C for 15 h.

Several experiments have been carried out to probe the mechanism of this reaction. Firstly, a cyclometalated Rh^{III} complex, **36**, can catalyze this amination reaction with an efficiency that is comparable to the method described herein, suggesting the relevancy of C–H activation [Eq. (1)]. Next, a series of control experiments were carried out on the conversion of hydroxylamine **4** into **3** [Eqs. (2), (3), and (4)]. Firstly, compound **4** was heated under air for 10 h and afforded **3** with 25% conversion [Eq. (2)]. Addition of 1-$AdCO_2H$ did not improve the conversion, suggesting an acid-promoted reaction mechanism is likely irrelevant [Eq. (3)]. A dramatic increase in reaction yield (90%) was observed when $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ was added, suggesting that a Rh^{III} complex promoted the conversion [Eq. (4)].

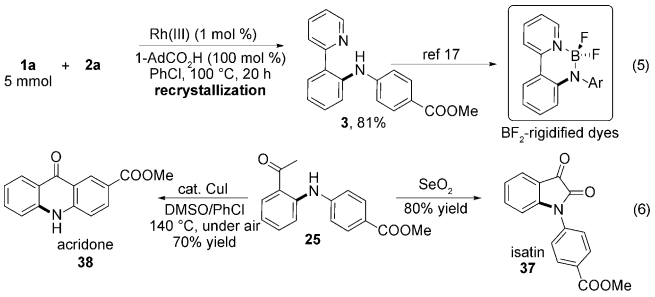


In view of the results presented above, we tentatively deduced the following mechanism (Scheme 5). The reaction of 2-phenylpyridine with the rhodium catalyst, and subsequent *ortho*-directed C–H bond activation, results in rhodacycle **A**.[15] Then, coordination and subsequent nucleophilic addition (or N=O insertion) takes place to afford Rh species **C**. Species **C** is protonated to produce the hydroxylamine **4** and the Rh^{III} catalyst. As previously reported,[13] nitroxide **D** is generated from **4** and oxygen. This transformation proceeds more quickly in the presence of the Rh^{III} complex.[16] Nitroxide **D** may undergo dimerization and subsequent fragmentation to give two aminyl radicals **E** and molecular oxygen, in a similar manner to the dimerization of peroxyl radicals. Finally, hydrogen abstraction from the solvent, or from **4**, delivers diarylamine **3**.



Scheme 5. Proposed mechanism (Ar = 4-COOMe-phenyl).

In order to demonstrate the strength of our methodology, an experiment was carried out on a larger scale [Eq. (5)]. Satisfyingly, by using only 1 mol% catalyst loading, the present amination reaction could be carried out with excellent efficiency to provide a diarylamine product, which can be used in fluorescent dyes.[17] In addition, diarylamines accessible by this C–H amination reaction have other synthetic utilities.[18] For example, 2-anilinoacetophenone (**25**) can be easily converted into isatin (**37**) and acridone (**38**) in one step [Eq. (6)].



Conclusion

In summary, we have developed an unprecedented Rh-catalyzed intermolecular addition of aryl C–H bonds to nitrosobenzenes, followed by cleavage of the resulting hydroxylamines in situ, to produce valuable and versatile diarylamines, which have versatile synthetic and medicinal utility. This reaction is compatible with air and water and can be carried out in the absence of external oxidants, thus providing an environmentally benign and straightforward synthesis of diarylamines that can be readily scaled-up. More importantly, this process may provide a new direction for attaching arylamine groups to aromatic rings.

Experimental Section

General procedure for the Rh-catalyzed C–H amination reaction

$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (2.5 mol%), 1-adamantane carboxylic acid (0.2 mmol), 2-phenylpyridine **1a** (0.2 mmol), methyl *p*-nitrosobenzoate (0.24 mmol), and PhCl (1 mL) were added to a sealed tube. The reaction mixture was stirred at 100 °C for 10 h, then EtOAc (6 mL) was added. Volatiles were removed under reduced pressure and the crude product was purified by column chromatography on silica gel.

Acknowledgements

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Keywords: C–H activation · diarylamines · isatin · nitrosobenzenes · rhodium

[1] Selected examples: a) A. Ricci, *Amino Group Chemistry: From Synthesis to the Life Sciences*, Wiley-VCH, Weinheim, **2008**; b) S. A. Lawrence, *Amines: Synthesis Properties and Applications*, Cambridge University, Cambridge, **2004**; c) D. R. Waring, G. Hallas, *The Chemistry and Application of Drugs*, Plenum, New York, **1990**; d) G. Thomas, *Medicinal Chemistry*, Wiley-VCH, Weinheim, **2000**.

[2] Selected examples: a) D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 6438; *Angew. Chem. Int. Ed.* **2008**, *47*, 6338; b) S. V. Ley, A. W. Thomas, *Angew. Chem.* **2003**, *115*, 5558; *Angew. Chem. Int. Ed.* **2003**, *42*, 5400; c) G. Evano, N. Blanchard, M. Toumi, *Chem. Rev.* **2008**, *108*, 3054; d) M. Kosugi, M. Kameyama, T. Migita, *Chem. Lett.* **1983**, 927; e) A. S. Guram, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 7901; f) F. Paul, J. Patt, J. F. Hartwig, *J. Am. Chem. Soc.* **1994**, *116*, 5969.

[3] For selected reviews, see: a) A. Armstrong, J. C. Collins, *Angew. Chem.* **2010**, *122*, 2332; *Angew. Chem. Int. Ed.* **2010**, *49*, 2282; b) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; c) J. Wencel-Delord, T. Droge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740.

[4] a) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790; b) H.-Y. Thu, W.-Y. Yu, C.-M. Che, *J. Am. Chem. Soc.* **2006**, *128*, 9048; c) T. Uemura, S. Imoto, N. Chatani, *Chem. Lett.* **2006**, *35*, 842; d) S. H. Cho, J. Y. Kim, S. Y. Lee, S. Chang, *Angew. Chem.* **2009**, *121*, 9291; *Angew. Chem. Int. Ed.* **2009**, *48*, 9127; e) D. Monguchi, T. Fujiwara, H. Furukawa, A. Mori, *Org. Lett.* **2009**, *11*, 1607; f) Q. Wang, S. L. Schreiber, *Org. Lett.* **2009**, *11*, 5178; g) J. Y. Kim, S. H. Cho, J. Joseph, S. Chang, *Angew. Chem.* **2010**, *122*, 10095; *Angew. Chem. Int. Ed.* **2010**, *49*, 9899; h) Q. Shuai, G. Deng, Z. Chua, D. S. Bohle, C.-J. Li, *Adv. Synth. Catal.* **2010**, *352*, 632; i) B. Xiao, T.-J. Gong, J. Xu, Z.-J. Liu, L. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 1466; j) A. John, K. M. Nicholas, *J. Org. Chem.* **2011**, *76*, 4158; k) L. D. Tran, J. Roane, O. Daugulis, *Angew. Chem.* **2013**, *125*, 6159; *Angew. Chem. Int. Ed.* **2013**, *52*, 6043; l) H. Zhao, Y. Shang, W. Su, *Org. Lett.* **2013**, *15*, 5106.

[5] a) K.-H. Ng, A. S. C. Chan, W.-Y. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 12862; b) T. Kawano, K. Hirano, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2010**, *132*, 6900; c) K. Sun, Y. Li, T. Xiong, J. Zhang, Q. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 1694; d) E. J. Yoo, S. Ma, T.-S. Mei, K. S. L. Chan, J.-Q. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 7652; e) N. Matsuda, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2011**, *13*, 2860; f) K.-H. Ng, Z. Zhou, W.-Y. Yu, *Org. Lett.* **2012**, *14*, 272; g) C. Grohmann, H. Wang, F. Glorius, *Org. Lett.* **2012**, *14*, 656; h) R.-J. Tang, C.-P. Luo, L. Yang, C.-J. Li, *Adv. Synth. Catal.* **2013**, *355*, 869; i) S. Yu, B. Wan, X. Li, *Org. Lett.* **2013**, *15*, 3706; j) C. Grohmann, H. Wang, F. Glorius, *Org. Lett.* **2013**, *15*, 3014; k) K.-H. Ng, Z. Zhou, W.-Y. Yu, *Chem. Commun.* **2013**, *49*, 7031; l) B. Zhou, J. Du, Y. Yang, Y. Li, *Org. Lett.* **2013**, *15*, 2934.

[6] J. Ryu, K. Shin, S. H. Park, J. Y. Kim, S. Chang, *Angew. Chem.* **2012**, *124*, 10042; *Angew. Chem. Int. Ed.* **2012**, *51*, 9904.

[7] a) B. Zhou, J. Du, Y. Yang, H. Feng, Y. Li, *Org. Lett.* **2013**, *15*, 6302; b) B. Zhou, J. Du, Y. Yang, H. Feng, Y. Li, *Org. Lett.* **2014**, *16*, 592.

[8] For recent reviews on Rh^{III}-catalyzed C–H activation, see: a) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212; b) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2012**, *45*, 814; c) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; d) F. W. Patureau, J. Wencel-Delord, F. Glorius, *Aldrichimica Acta* **2012**, *45*, 31; e) S. Chiba, *Chem. Lett.* **2012**, *41*, 1554; f) C. Zhu, R. Wang, J. R. Falck, *Chem. Asian J.* **2012**, *7*, 1502.

[9] For selected Rh^{III}-catalyzed addition of aryl C–H bonds to C=N and C=O bonds, see: a) A. S. Tsai, M. E. Tauchert, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2011**, *133*, 1248; b) Y. Li, B.-J. Li, W.-H. Wang, W.-P. Huang, X.-S. Zhang, K. Chen, Z.-J. Shi, *Angew. Chem.* **2011**, *123*, 2163; *Angew. Chem. Int. Ed.* **2011**, *50*, 2115; c) M. E. Tauchert, C. D. Incarvito, A. L. Rheingold, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2012**, *134*, 1482; d) L. Yang, C. A. Correia, C.-J. Li, *Adv. Synth. Catal.* **2011**, *353*, 1269; e) C. Zhu, W. Xie, J. R. Falck, *Chem. Eur. J.* **2011**, *17*, 12591; f) B. Zhou, Y. Yang, Y. Li, *Chem. Commun.* **2012**, *48*, 5163; g) Y. Li, X.-S. Zhang, K. Chen, K.-H. He, F. Pan, B.-J. Li, Z.-J. Shi, *Org. Lett.* **2012**, *14*, 636; h) Y. Yang, B. Zhou, Y. Li, *Adv. Synth. Catal.* **2012**, *354*, 2916; i) W. Hou, B. Zhou, Y. Yang, H. Feng, Y. Li, *Org. Lett.* **2013**, *15*, 1814; j) B. Zhou, W. Hou, Y. Yang, Y. Li, *Chem. Eur. J.* **2013**, *19*, 4701; k) B. Zhou, Y. Yang, S. Lin, Y. Li, *Adv. Synth. Catal.* **2013**, *355*, 360 – 364; l) Y. Lian, R. B. Bergman, L. D. Lavis, J. A. Ellman, *J. Am. Chem. Soc.* **2013**, *135*, 7122.

[10] For selected Rh^{III}-catalyzed C–H functionalization by using alkynes and alkenes as substrates, see: a) B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, *J. Am. Chem. Soc.* **2013**, *135*, 468; b) H. Wang, N. Schroder, F. Glorius, *Angew. Chem.* **2013**, *125*, 5495; *Angew. Chem. Int. Ed.* **2013**, *52*, 5386; c) H. Wang, C. Grohmann, C. Nimphius, F. Glorius, *J. Am. Chem. Soc.* **2012**, *134*, 19592; d) W. Zhen, F. Wang, M. Zhao, Z. Du, X. Li, *Angew. Chem.* **2012**, *124*, 11989 – 11993; *Angew. Chem. Int. Ed.* **2012**, *51*, 11819; e) B.-J. Li, H.-Y. Wang, Q.-L. Zhu, Z.-J. Shi, *Angew. Chem.* **2012**, *124*, 4014; *Angew. Chem. Int. Ed.* **2012**, *51*, 3948; f) D. Wang, F. Wang, G. Song, X. Li, *Angew. Chem.* **2012**, *124*, 12514; *Angew. Chem. Int. Ed.* **2012**, *51*, 12348; g) M. V. Pham, B. Ye, N. Cramer, *Angew. Chem.* **2012**, *124*, 10762; *Angew. Chem. Int. Ed.* **2012**, *51*, 10610; h) J. Zhang, T.-P. Loh, *Chem. Commun.* **2012**, *48*, 11232; i) B. Ye, N. Cramer, *Science* **2012**, *338*, 504; j) F. W. Patureau, T. Besset, N. Kuhl, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2154; k) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449; l) M. P. Huestis, L. Chan, D. R. Stuart, K. Fagnou, *Angew. Chem.* **2011**, *123*, 1374; *Angew. Chem. Int. Ed.* **2011**, *50*, 1338; m) F. W. Patureau, F. Glorius, *Angew. Chem.* **2011**, *123*, 2021; *Angew. Chem. Int. Ed.* **2011**, *50*, 1977; n) P. C. Too, Y.-F. Wang, S. Chiba, *Org. Lett.* **2010**, *12*, 5688; o) S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350; p) T. K. Hyster, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 10565; q) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585; r) N. Guimond, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 12050; s) N. Umeda, H. Tsurugi, T. Satoh, M. Miura, *Angew. Chem.* **2008**, *120*, 4083; *Angew. Chem. Int. Ed.* **2008**, *47*, 4019; t) D. R. Stuart, M. Bertrand-Laperle, K. M. N. Burgess, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 16474; u) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407; v) K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.* **2007**, *72*, 5362.

[11] For Rh^{III}-catalyzed coupling with diazo compounds, aziridines, cyano and diphenyl disulfide, see: a) W.-W. Chan, S.-F. Lo, Z. Zhou, W.-Y. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 13565; b) T. K. Hyster, K. E. Ruhl, T. Rovis, *J. Am. Chem. Soc.* **2013**, *135*, 5364; c) Z. Shi, D. C. Koester, M. Boultadakis-Arapinis, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 12204; d) X. Li, S. Yu, F. Wang, B. Wan, X. Yu, *Angew. Chem.* **2013**, *125*, 2637; *Angew. Chem. Int. Ed.* **2013**, *52*, 2577; e) T.-J. Gong, B. Xiao, W.-M. Cheng, W. Su, J. Xu, Z.-J. Liu, L. Liu, Y. Fu, *J. Am. Chem. Soc.* **2013**, *135*, 10630; f) Y. Yang, W. Hou, L. Qin, J. Du, H. Feng, B. Zhou, Y. Li, *Chem. Eur. J.* **2014**, *20*, 416.

[12] For Rh-catalyzed arene C–H amidation with sulfonyl azides, see: a) J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim, S. Chang, *J. Am. Chem. Soc.* **2012**, *134*, 9110; b) J. Shi, B. Zhou, Y. Yang, Y. Li, *Org. Biomol. Chem.* **2012**, *10*, 8953; c) D. G. Yu, M. Suri, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 8802; For Ru-catalyzed C–H amidation with sulfonyl azides, see: d) V. S. Thirunavukkarasu, K. Raghuvanshi, L. Ackermann, *Org. Lett.* **2013**, *15*, 3286; e) J. Kim, J. Kim, S. Chang, *Chem. Eur. J.* **2013**, *19*, 7328; f) M. R. Yadav, R. K. Rit, A. K. Sahoo, *Org. Lett.* **2013**, *15*, 1638; g) Q.-Z. Zheng, Y.-F. Liang, C. Qin, N. Jiao, *Chem. Commun.* **2013**, *49*, 5654; For intermolecular aldehyde C–H amidation with sulfonyl azides, see: h) B. Zhou, Y. Yang, J. Shi, H. Feng, Y. Li, *Chem. Eur. J.* **2013**, *19*, 10511.

[13] A. R. Forrester, J. D. Fullerton, G. McConnachie, *J. Chem. Soc. Perkin Trans. 1* **1983**, 1759.

[14] CCDC-958065 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] a) L. Li, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 12414; b) L. Li, W. Brennessel, W. D. Jones, *Organometallics* **2009**, *28*, 3492.

[16] High-oxidation-value metal salts can help produce radical with oxygen, see: a) T. Taniguchi, Y. Sugiura, H. Zaimoku, H. Ishibashi, *Angew. Chem.* **2010**, *122*, 10352; *Angew. Chem. Int. Ed.* **2010**, *49*, 10154; b) T. Taniguchi, H. Zaimoku, H. Ishibashi, *Chem. Eur. J.* **2011**, *17*, 4307; c) Y. Su, X. Sun, G. Wu, N. Jiao, *Angew. Chem.* **2013**, *125*, 9990 – 9994: Angew. Chem. Int. Ed. **2013**, 52, 9808.

[17] J. F. Araneda, W. E. Piers, B. Heyne, M. Parvez, R. McDonald, *Angew. Chem.* **2011**, *123*, 12422; *Angew. Chem. Int. Ed.* **2011**, *50*, 12214.

[18] a) Y. Liu, H. Chen, X. Hu, W. Zhou, G.-J. Deng, *Eur. J. Org. Chem.* **2013**, 4229; b) W. Zhou, Y. Yang, Y. Liu, G.-J. Deng, *Green Chem.* **2013**, *15*, 76.

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FULL PAPER

C–H Activation

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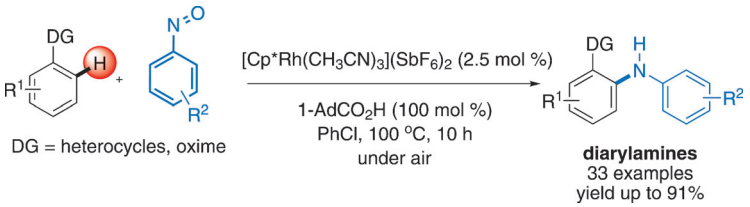
Rhodium-Catalyzed Direct Amination of Arenes with Nitrosobenzenes: A New Route to Diarylamines



A Rh^{III}-catalyzed addition of aryl C–H bonds to nitrosobenzenes, followed by cleavage of the resulting hydroxylamines in situ, is reported (see scheme). Different directing groups, such as N-based heterocycles and ketoximes, can be used in this C–H amination process, providing valuable diarylamines in excellent yields. Most importantly, this process provides a new method for attaching arylamine groups to aromatic rings.