ORGANOMETALLICS

Nickel Dual Photoredox Catalysis for the Synthesis of Aryl Amines

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S Supporting Information

ABSTRACT: In this work, a new dual photoredox nickel catalysis system has been utilized for the synthesize of aryl amines. Previously, our group has shown that a nickel catalyst in conjunction with a photosensitizer and a sacrificial electron donor can cross-couple C-C bonds via photoredox-assisted reductive coupling. Here we have built upon that system to develop a redox-neutral cross-coupling system for the formation of C-N bonds. The catalytic system is composed of just a nickel cross-coupling catalyst, a Ru photocatalyst, and base and is capable of coupling amines with aryl halides in good to excellent yields. Furthermore, it was found that these reactions are functional under ambient conditions with catalyst



loadings of 1 mol %. Spectroscopic studies provide support that this amination mechanism proceeds via a nitrogen-based radical intermediate. This N-radical mechanism offers direct synthetic access to di- and triaryl amines from nickel photocatalysis.

INTRODUCTION

Thermally controlled cross-coupling reactions rely on ligand exchange mechanisms, such as transmetalation. This synthetic approach has continued to advance, but some cross-coupling reactions and products have been limited under thermal control.^{1,2} The development of new cross-coupling methodologies, which may avoid ligand exchange mechanisms, have been achieved recently. These catalytic methodologies, such as reductive coupling³ and photoredox coupling,^{4–6} have shown the ability to perform previously unachieved cross-coupling reactivity. Of specific importance to this report, dual photoredox catalysis enables routes for previously unattainable small-molecule activations and bond-forming reactions. Dual photoredox catalysis utilizes these single-electron transfers to activate a secondary transition-metal catalyst for small-molecule activations and bond-forming reactions.

Predominately, dual photoredox systems utilize nickel crosscoupling catalysts. Proposed mechanisms involve nickel catalysts in oxidation states that range from Ni⁰ to Ni^{III}. At room temperature, it has been shown that the Ni^{III} oxidation state is necessary to promote product formation through reductive elimination.^{20,21} For dual photoredox cross-coupling from nickel–polypyridyl catalysts, multiple routes to form the important Ni^{III} oxidation state have been proposed. One proposed route is the oxidative addition of a carbon electrophile to a Ni^I intermediate (Figure 1a).^{8,14,22–24} Another route proposes that the Ni^{III} intermediate is formed via photocatalyst oxidation of a Ni^{II} intermediate (Figure 1b).^{10,25} The Ni^I oxidative addition and Ni^{II} oxidation routes both tend to operate in mechanisms that rely on ligand exchange reactions to ultimately form the desired cross-coupled product. Conversely, the Ni^{III} intermediate has been shown to form via a reaction between a carbon radical and a Ni^{II} intermedi-



Figure 1. Comparison of the proposed reactions for the formation of a Ni^{III} oxidation state during dual photoredox catalysis.

ate,^{4,5,12,13,26} which was also observed in our laboratory (Figure 1c).²⁷ This radical reactivity avoids ligand exchange mechanisms and can lead to previously unexplored product formation and reactivity.

Traditional amination pathways use palladium phosphane catalysts to form new C–N bonds and operate through Pd⁰/Pd^{II} oxidation states.²⁸ The phosphane ligands require precise electron-donating/-withdrawing properties and steric encumbrance to promote product formation via reductive elimination from the Pd^{II} intermediate.^{28–30} Utilizing dual photoredox nickel catalysis with simple ligand environments for the construction of C–N bonds, therefore, is highly desirable. In addition, the range of electrophiles amenable to nickel cross-coupling reactions should allow for a wide diversity of aminated products.^{31–33} Reactions that construct new C–N bonds are

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also of great importance to pharmaceutical synthesis, constituting roughly 27% of pharmaceutical reactions.³

Recently dual photoredox nickel catalysis for the synthesis of diaryl amines has been achieved.^{23,25} Both studies were able to achieve diaryl amine products using ligandless nickel salts as the cross-coupling catalysts, which illustrates the advantages of dual photoredox cross-coupling in comparison to thermally controlled reactions. Furthermore, the C-N photoredox coupling for the synthesis of aryl amines has been achieved using organic dyes.³⁵ For one of the studies, generation of the important Ni^{III} intermediate was proposed to occur through oxidation of a Ni^{II} intermediate, as illustrated in Figure 1b.²⁴ Formation of amine radicals was not proposed for this mechanism. For the second study, it was postulated that formation of the Ni^{III} intermediate occurred through oxidative addition of aryl halides to a Ni^I intermediate, as shown in Figure 1a.²³ Computational insight into possible reaction mechanisms for these systems was also recently reported.^{24,36} Comparison of these mechanisms to our work is discussed in further detail later in this paper.

RESULTS AND DISCUSSION

To optimize our dual photoredox catalytic system for the construction of C–N bonds and the synthesis of diaryl amines, cross-coupling between 4-methoxyaniline and iodobenzene was chosen as a test reaction. Blue light irradiation of the coupling substrates in the presence of the $[Ni(tpy)(py)](PF_3)_2$ crosscoupling catalyst (tpyNi),²⁷ Ru(phen)₃²⁺ photocatalyst, and a potassium phosphate base in acetonitrile resulted in 76% yield of the desired cross-coupled diaryl amine product (Table 1, row 1). It was observed that a small excess of aryl halide led to greater product yields. This result is consistent with previously reported coupling between aryl halides and in situ generated radicals.²⁷ These reactions were set up on the benchtop without

Table	1.	Optimization	of	Reaction	Conditions ⁴



^aThe solvent was acetonitrile (MeCN) and base was K₃PO₄ unless otherwise stated. Abbreviations: tpy, 2,2':6',2"-terpyridine; phen, 1,10phenanthroline; (dF-CF₃-ppy), 2-(2,4-difluorophenyl)-5-(trifluoromethyl)phenylpyridine; dtbpy, 4,4'-ditert-butyl-2,2'-bipyridine. Reactions were carried out for 24 h.

DMF instead of MeCN

degassing, illustrating the ease of reaction setup for this approach.

Variations of the optimized conditions are shown in Table 1. Using $Ir(ppy)_2(dtbpy)^+$ as the photocatalyst resulted in comparable yields in comparison to Ru(phen)₃²⁺, likely due to the similar excited state oxidation potentials of the two photocatalysts. Using the highly oxidizing Ir(dF-CF₃ $ppy)_2(dtbpy)^+$ photocatalyst led to drastically lower product yields. Attempting to perform the experiment with NiCl₂ and 2,2':6',2"-terpyridine ligand added instead of the preformed catalyst did not produce product, as has been observed with this nickel salt/ligand combination.²⁷ Lack of C-N cross-coupling from simple nickel salts is, however, a deviation from previously reported nickel dual photoredox C-N coupling.^{23,25} Changing the base from K₃PO₄ to triethanolamine or changing the reaction solvent resulted in no product formation. Complete removal of any of the catalytic components-nickel catalyst, photocatalyst, base, or light-also led to the lack of product formation. Finally, the addition of water to the reaction mixture did not increase or negatively affect the product yield; hence, the use of dried solvents is not necessary for this catalytic system.

With the optimized reaction conditions in hand, we explored the substrate scope for this catalytic system. First, pmethoxyaniline was used as a general and efficient amine coupling partner to examine the range of possible aryl coupling partners. Aryl iodides resulted in greater product yields in comparison to aryl bromides, which is consistent with previously reported nickel dual photoredox aryl amine ²³ Figure 2 shows that cross-coupling yields up to syntheses.²



Figure 2. Catalytic dual photoredox cross-coupling between pmethoxyaniline and aryl halides. Conditions: 100 mM aniline, 200 mM aryl halide in 5 mL of acetonitrile. The mole percentages and percent yields are based on limiting reagent.

93% can be achieved by varying the aryl iodide. In every case, further reactions of the diaryl amine products to form triaryl amines were not observed and no homocoupled biaryl products were observed. Leftover starting reactants, after the 24 h reaction time, were observed with GC/MS analysis of the reaction mixtures. Both electron-donating and -withdrawing groups are tolerated. Good yields were obtained regardless of functional group position, as seen with the para (2)- and metapositioned (3) iodoanisole substrates. Ortho-substituted aryl iodides such as 2-iodotoluene (4), however, exhibited lower yields than p-iodotoluene (5). It is suspected that these lower

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yields can partially be attributed to steric effects; however, the sterically hindered 1-iodonaphthalene did lead to good yields (9). Therefore, the electron-donating/-accepting abilities of the methyl group versus the increased aromaticity of the naphthyl ring also has an effect on product yield. Coupling of heteroaryl iodides with 4-methoxyaniline was also successful (7 and 8).

A variety of amine coupling partners were also well tolerated by this catalytic system. Figure 3 shows that ortho, meta, and



Figure 3. Catalytic dual photoredox cross-coupling between aryl iodide and various aniline substrates. Conditions: 100 mM anilines, 200 mM aryl iodide in 5 mL of acetonitrile. The mole percentages and percent yields are based on limiting reagent.

para substitutions on aniline substrates all result in good yields (1, 10, and 11). Highly substituted aniline substrates were also successful (12). These reactions were also capable of coupling complex heterocycles, such as 3,4-methylenedioxyaniline, as amine coupling partners (15). Coupling of 4-chloroaniline, which contains a synthetically useful chloro functional group, was moderately tolerated (16). The possible C-C crosscoupled side product for that reaction was not observed. Crosscoupling involving sulfonamides was also successful (17). Furthermore, starting with secondary amines as coupling partners led to the formation of tertiary amine products, as shown with products 18-21. Products 18 and 19 show that amines containing both aryl groups and aliphatic groups are capable of being utilized in C-N coupling reactions. A triaryl amine, product 20, can be formed with 71% yield on starting with the diaryl amine. Finally, dibenzyl amine was also a suitable cross-coupling partner, forming the trisubstituted amine 21 in good yield. Thus, this is the first dual photoredox nickel catalysis system capable of the synthesis of both bi- and triaryl amine products.

To gain insight into how our catalytic system successfully performs C-N cross-coupling reactions, we examined the interaction between the amine substrates and the Ru photoredox catalyst. As discussed in the Introduction, gaining

access to a Ni^{III} oxidation state is essential to forming crosscoupled products during room-temperature dual photoredox catalysis. Three mechanistic routes for the formation of a Ni^{III} oxidation state have been proposed (Figure 1). In our previous work, we have observed that a carbon-based radical formed during photoredox cross-coupling catalysis was essential for mediating the oxidation state of the **tpyNi** catalyst.²⁷ With this radical-based mechanism in mind, we set to examine the interaction between the amine substrates and the Ru photoredox catalyst. Recently, during cyclization reactions, the Knowles group has shown that nitrogen-based radicals can be formed via photoredox oxidative proton-coupled electron transfer (PCET).³⁷ Thus, we aimed to explore the possibility that forming amine radicals is a key step for our dual photoredox catalytic system.

Various fluorescence quenching experiments involving combinations of the Ru photocatalyst in the presence of pmethoxyaniline, K₃PO₄ base, and the entire catalytic reaction mixture were performed. A Stern-Volmer analysis showed that the Ni(II) catalyst does not quench the photocatalyst (Figure SI-2). Furthermore, the base alone does not quench the Ru photocatalyst (Figure SI-3). The *p*-methoxyaniline substrate in both the absence and presence of base, however, did quench the photocatalyst (Figures SI-3 and SI-4). The Stern-Volmer plots for amine quenching exhibited a linear fit, indicating the quenching was first order with respect to the aniline substrate. These data suggest that electron transfer occurs directly between the aniline substrate and the photocatalyst and that PCET does not appear to be the dominant pathway. Instead, it is proposed that electron transfer between the aniline substrate and the photocatalyst occurs first, followed by deprotonation of the oxidized aniline by the added base. This electron transfer followed by proton transfer mechanism for the formation of nitrogen radicals has been previously reported.^{38,39}

To test if quenching of the photocatalyst by the amine substrate was catalytically feasible, quenching experiments were performed using conditions identical with the optimized reaction conditions. Fluorescence quenching was once again observed under optimized reaction conditions (Figure SI-5). The slope of the Stern–Volmer plot for the entire reaction mixture was similar to the slope of the Stern–Volmer plot obtained from the photocatalyst in the presence of the aniline substrate plus base. The similarity in slopes indicates that quenching of the photocatalyst by the aniline substrate is catalytically feasible within the reaction mixture.

A likely mechanism for this catalytic system is shown in Figure 4. The Ru photocatalyst absorbs a photon of light to generate a long-lived excited state (Ru^{II*}). The blue light source has a maximum intensity at 480 nm, which overlaps well with the Ru photocatalyst absorbance spectrum. The Ni catalyst does not absorb light in the visible region (Figure S1); thus, Ni catalyst light absorbance is not expected to play a role in the operative mechanism.

The excited state Ru^{II*} is then reductively quenched by the aniline substrate to concurrently generate a reduced photocatalyst (Ru^{I}) and an oxidized amine. Formation of amine radicals is supported by the fluorescence quenching studies and was further supported by the fact that electron-rich aniline substrates are more efficient coupling partners in comparison to electron-deficient anilines. After oxidation of the aniline substrate, the acidity of the amine group increases, leading to subsequent deprotonation by the added base. The reduced photocatalyst, Ru^{I} , then reduces the nickel catalyst for both the



Figure 4. Proposed mechanism for dual photoredox C–N cross-coupling catalysis via an amine radical.

Ni(II/I) and Ni(I/0) couples. The reductive driving force of the Ru(II/I) couple is -1.36 V vs the saturated calomel electrode, while the Ni(I/0) couple requires -1.3 V.²⁷ Oxidative addition of an aryl iodide to Ni⁰ in step 3 generates a Ni^{II}-Ph intermediate. Steps 2 and 3 are consistent with previously reported reactivity between **tpyNi** and aryl halides.²⁷ In addition, the halide lost from the aryl group is likely picked up by potassium from the added base to generate a potassium iodide salt, as has been observed.²⁷ The Ni^{II}-Ph intermediate then reacts with the aniline radical to generate the important Ni^{III} intermediate in step 4, followed by reductive elimination in step 5 to form the desired C-N cross-coupled product. Step 4 in the proposed cycle is analogous to the reports summarized in Figure 1c.

This proposed mechanism differs from each of the previously proposed nickel dual photoredox mechanisms for the formation of biaryl amines. The MacMillan group reported that the formation of the important Ni^{III} intermediate occurred via oxidation of a Ni^{II}-amido complex by an iridium photocatalyst, as shown in Figure 1b.²⁵ That mechanism relied on ligand exchange between the amine substrates and halide groups of the nickel center and did not propose the formation of an amine radical. In addition, the formation of aryl amines was only observed when amines containing α -hydrogens were present. Recent computational work gave insight into the requirement for α -hydrogen-containing heterocycles.³⁶ In that paper, the authors propose that the hydrogen atom transfer reagent DABCO generates a pyrrolidine radical that helps generate a Ni⁰ intermediate capable of activating aryl halides.³ The catalytic system reported in this paper does not require substrates containing α -hydrogens or the addition of hydrogen atom transfer reagents. Instead, this catalytic system was able to directly synthesize bi- and triaryl amines with only the addition of a common base to the dual photoredox catalysts.

In another study by researchers at AstraZeneca,²³ fluorescence quenching studies provided evidence for the formation of amine radicals during dual photoredox biaryl synthesis, as was observed in this study. The authors, however, proposed that the amine radical reacted directly with the Ni⁰ intermediate to generate a Ni¹-amine intermediate. It was then proposed that the Ni¹ intermediate was capable of activating aryl halides in a reaction such as that shown in Figure 1a. Radical reactivity with Ni⁰ complexes and aryl halide activation by Ni¹ intermediates has been supported by computational work.²⁴ In addition, fluorescence quenching of their photocatalyst also occurred in the presence of the triethyl amine base used in their study, which is commonly seen with this amine base.²⁷ While our proposed mechanism and their proposed mechanism differ just slightly, the mechanistic differences once again lead to a difference in accessible products. Both studies were able to synthesize a variety of diaryl amines including sulfonamides; however, the previous study reports an inability to synthesize triphenyl amine and only a 9% yield for the formation of *N*-methyl-*N*-phenylaniline, whereas the catalytic system reported in this paper was able to synthesize those products with 71% and 83% yields, respectively.

In conclusion, the differing aspects of the three reports on nickel dual photoredox catalysis for the formation of aryl amines show both the versatility and range of chemistries that can be achieved using this approach. The catalytic system in this report utilizes a Ru photocatalyst to generate amine radicals for cross-coupling reactions with aryl iodide substrates. This approach is amenable to a variety of both aryl iodide and amine coupling partners and can be set up and performed under ambient conditions. Both biaryl and tertiary amine products can be accessed using this approach, which operates with only added base and 1 mol % catalyst loadings.

EXPERIMENTAL SECTION

Instrumentation. All separations were conducted on a Reveleris X2 flash chromatography system using a 40 μ M silica column or via preparative-scale TLC. Solvents used for purification were ethyl acetate and hexane of ACS grade or better (\geq 99%) and were used without further purification.

¹H NMR spectroscopy was performed using a 300 MHz instrument using deuterated chloroform as the solvent with a calibrated peak at 7.26 ppm. ¹³C NMR was conducted on a 300 MHz instrument set to a frequency of 75 MHz using chloroform as the solvent and a calibrated solvent peak at 77.33 ppm. The light source used for all experiments was a 34 W Kessil H150W-BLUE light exciting at 400–500 nm with a maximum intensity at 480 nm. The light source was placed 6 in. from the reaction vials with aluminum foil located 2 in. behind the vials to redirect incident light. The temperature was monitored during the reactions, and no increase above room temperature was observed.

Emission spectra were acquired on an Edinburgh FSS fluorescence spectrometer equipped with a 150 W continuous wave xenon lamp source for excitation. Emission measurements on degassed solution samples were collected on solutions of appropriate materials inside a 1.0 cm quartz cuvette using the SC-05 standard cuvette module.

General Procedure for Photoredox-Assisted Amination Reactions. In a 12 mL glass vial with a TFE/SIL O/T cap were placed $[Ni(tpy)(py)(MeCN)_2]PF_6$ (0.005 mmol, 1% loading), $Ru(phen)_3^{2+}$ (0.005 mmol, 1% loading), amine (0.5 mmol), aryl iodide (1.0 mmol), and base (0.5 mmol) and dissolved in 5 mL of acetonitrile. The vial was then placed in front of the blue LED light source on a stir plate and was irradiated for 24 h with stirring. After 24 h, the solution was then separated via flash chromatography using ethyl acetate and hexanes. The isolated products were then analyzed via ¹H NMR and ¹³C NMR to confirm purity. Standard chemical safety procedures should be used with all chemicals, but it is worth noting that inhalation of *p*-methoxyaniline can be fatal; thus, a mask is required while handling that solid substrate.

Stern–Volmer Experiments. Fluorescence quenching experiments were performed with N₂-purged solutions of 5×10^{-6} M Ru(phen)₃²⁺ in acetonitrile at room temperature. The solutions were irradiated at 480 nm, and fluorescence was measured at 598 nm. Each peak intensity is the average of three experimental spectra. Data can be found in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00121.

Fluorescence quenching data, ¹H and ¹³C NMR data, and references to previously reported products (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Terao, J.; Kambe, N. Acc. Chem. Res. 2008, 41, 1545-1554.
- (2) Jana, R.; Pathak, T. P.; Sigman, M. S. Chem. Rev. 2011, 111,
- 1417–1492.
- (3) Weix, D. J. Acc. Chem. Res. 2015, 48, 1767–1775.
- (4) Tellis, J. C.; Primer, D. N.; Molander, G. A. Science 2014, 345, 433–436.
- (5) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. *Science* **2014**, *345*, 437–440.
- (6) Ye, Y.; Sanford, M. S. J. Am. Chem. Soc. 2012, 134, 9034–9037.
 (7) Skubi, K. L.; Blum, T. R.; Yoon, T. P. Chem. Rev. 2016, 116, 10035–10074.
- (8) Jouffroy, M.; Primer, D. N.; Molander, G. A. J. Am. Chem. Soc. 2016, 138, 475-478.
- (9) Jeffrey, J. L.; Petronijević, F. R.; MacMillan, D. W. C. J. Am. Chem. Soc. 2015, 137, 8404-8407.
- (10) Terrett, J. A.; Cuthbertson, J. D.; Shurtleff, V. W.; MacMillan, D. W. C. *Nature* **2015**, *524*, 330–334.
- (11) Ventre, S.; Petronijevic, F. R.; MacMillan, D. W. C. J. Am. Chem. Soc. 2015, 137, 5654–5657.
- (12) Zhang, P.; Le, C. C.; MacMillan, D. W. C. J. Am. Chem. Soc. 2016, 138, 8084–8087.
- (13) Noble, A.; McCarver, S. J.; MacMillan, D. W. C. J. Am. Chem. Soc. 2015, 137, 624-627.
- (14) Patel, N. R.; Molander, G. A. J. Org. Chem. 2016, 81, 7271-7275.
- (15) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. J. Org. Chem. 2016, 81, 6898-6926.
- (16) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. Acc. Chem. Res. **2016**, *49*, 1429–1439.
- (17) Kalyani, D.; McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S. J. Am. Chem. Soc. **2011**, 133, 18566–18569.
- (18) Zoller, J.; Fabry, D. C.; Ronge, M. A.; Rueping, M. Angew. Chem., Int. Ed. 2014, 53, 13264–13268.
- (19) Shu, X.-z.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D. J. Am. Chem. Soc. 2014, 136, 5844-5847.
- (20) Han, R.; Hillhouse, G. L. J. Am. Chem. Soc. 1997, 119, 8135-8136.
- (21) Macgregor, S. A.; Neave, G. W.; Smith, C. Faraday Discuss. 2003, 124, 111–127.
- (22) Vara, B. A.; Patel, N. R.; Molander, G. A. ACS Catal. 2017, 7, 3955–3959.
- (23) Oderinde, M. S.; Jones, N. H.; Juneau, A.; Frenette, M.; Aquila, B.; Tentarelli, S.; Robbins, D. W.; Johannes, J. W. Angew. Chem., Int.

Ed. 2016, 55, 13219-13223.

- (24) Gutierrez, O.; Tellis, J. C.; Primer, D. N.; Molander, G. A.; Kozlowski, M. C. J. Am. Chem. Soc. **2015**, 137, 4896–4899.
- (25) Corcoran, E. B.; Pirnot, M. T.; Lin, S.; Dreher, S. D.; DiRocco, D. A.; Davies, I. W.; Buchwald, S. L.; MacMillan, D. W. C. *Science* **2016**, 353, 279–283.
- (26) Biswas, S.; Weix, D. J. J. Am. Chem. Soc. 2013, 135, 16192–16197.
- (27) Paul, A.; Smith, M. D.; Vannucci, A. K. J. Org. Chem. 2017, 82, 1996–2003.
- (28) Wolfe, J. P.; Wagaw, S.; Marcoux, J. F.; Buchwald, S. L. Acc. Chem. Res. 1998, 31, 805-818.
- (29) Surry, D. S.; Buchwald, S. L. Angew. Chem., Int. Ed. 2008, 47, 6338–6361.
- (30) Ruiz-Castillo, P.; Buchwald, S. L. Chem. Rev. 2016, 116, 12564–12649.
- (31) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299–309.

(32) Netherton, M. R.; Fu, G. G. Adv. Synth. Catal. 2004, 346, 1525–1532.

- (33) Dander, J. E.; Garg, N. K. ACS Catal. 2017, 7, 1413-1423.
- (34) Roughley, S. D.; Jordan, A. M. J. Med. Chem. 2011, 54, 3451–3479.
- (35) Du, Y.; Pearson, R. M.; Lim, C. H.; Sartor, S. M.; Ryan, M. D.; Yang, H.; Damrauer, N. H.; Miyake, G. M. *Chem. - Eur. J.* **2017**, *23*, 10962–10968.
- (36) Qi, Z.-H.; Ma, J. ACS Catal. 2018, 8, 1456-1463.
- (37) Miller, D. C.; Choi, G. J.; Orbe, H. S.; Knowles, R. R. J. Am. Chem. Soc. 2015, 137, 13492–13495.
- (38) Chen, J. R.; Hu, X. Q.; Lu, L. Q.; Xiao, W. J. Chem. Soc. Rev. 2016, 45, 2044–2056.
- (39) Xiong, T.; Zhang, Q. Chem. Soc. Rev. 2016, 45, 3069-3087.