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Nickel-Catalyzed Electrooxidative C–H Amination: Support for Nickel(IV)

Shou-Kun Zhang,[a] Ramesh C. Samanta,[a] Nicolas Sauermann,[a] and Lutz Ackermann*[a]

Abstract: Nickel-catalyzed electrochemical C–H aminations were accomplished by chemo- and position-selective C–H activation with ample scope. Detailed mechanistic studies highlighted a facile C–H cleavage with unique chemo-selectivity, while cyclovoltammetric analysis provided support for a nickel(II/III/IV) manifold.

Combining metal-catalyzed C–H activation[1] with electrocatalysis[2] holds transformative potential for molecular syntheses,[3] because it circumvents the use of toxic and expensive metal oxidants.[4] The use of electricity as formal oxidant for C–H activation is likewise attractive since it allows the sustainable use of renewable energy. While this approach considerably improved the atom-economy of C–H activation, advances were until very recently largely limited to the precious 4d metals palladium,[5] rhodium,[6] ruthenium[7] and iridium.[8] In sharp contrast, only very recently we have unraveled the potential of cobalt catalysts for electrochemical C–H functionalizations,[9] which has proven instrumental for cobalt-mediated transformations.[10] Despite of this indisputable progress, electrochemical C–H nitrogenation with the less toxic base metal nickel[11,12] has thus far proven elusive. As a direct consequence, within our program[13] on nickel-catalyzed[14] C–H activation,[15] we became attracted to probing the opportunities of joining nickel catalysis with electrochemical C–H activation, the results of which we report herein. Key features of our findings include a) first nickel-catalyzed electrochemical C–H aminations, b) chemical oxidant-free C–H nitrogenations with cyclic and more challenging acyclic amines, and c) key mechanistic insights into nickel-electrocatalyzed C–H activation. It is thus noteworthy that our studies highlight a distinct working mode by fast C–H scission, involving a scarce nickel(IV) intermediate.

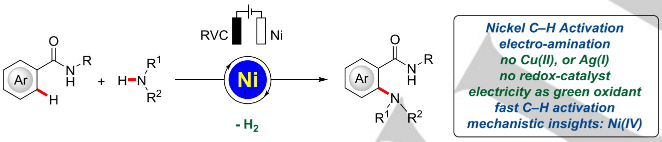
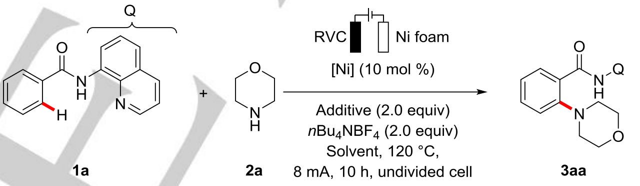


Figure 1. Nickel-catalyzed electrochemical C–H nitrogenation by nickel(IV).

We commenced our studies by probing various reaction conditions for the envisioned electrooxidative C–H amination by nickel catalysis (Table 1; Tables S–1-S–5 in the Supporting Information).[16] After considerable orienting experimentation, we observed that the desired C–H activation could be realized with $Ni(OAc)_2 \cdot 4H_2O$ as the catalyst (entry 1). Among various additives and solvents, NaOPiv and DMA emerged as being optimal, respectively (entries 2-7). It is noteworthy that, in contrast to cobalt catalysis,[10c] biomass-derived solvent GVL failed to provide the desired product **3aa** (entry 5). Subsequent adjustment of the reaction conditions, including additive stoichiometry and concentration, further improved the performance of the nickel/electro-catalysis (entries 8-11). The key role of the electricity (entry 12) and the nickel complex (entry 13) was confirmed by control experiments. It is noteworthy that an additional redox-mediator was not required for the nickel-catalyzed electroamination, contrasting with very recent copper catalysis.[14]

Table 1. Optimization of the Electrochemical Nickel-Catalyzed C–H Amination.[a]



1a **2a** **3aa**

Entry	Solvent	Additive	[Ni]	**3aa** [%]
1	DMA	---	$Ni(OAc)_2 \cdot 4H_2O$	10
2	DMA	PivOH	$Ni(OAc)_2 \cdot 4H_2O$	35
3	DMA	NaOPiv	$Ni(OAc)_2 \cdot 4H_2O$	55
4	DMA	Na_2CO_3	$Ni(OAc)_2 \cdot 4H_2O$	24
5	GVL	NaOPiv	$Ni(OAc)_2 \cdot 4H_2O$	---
6	NMP	NaOPiv	$Ni(OAc)_2 \cdot 4H_2O$	44
7	DMF	NaOPiv	$Ni(OAc)_2 \cdot 4H_2O$	22
8	DMA	NaOPiv	$Ni(OAc)_2 \cdot 4H_2O$	20[b]
9	DMA	NaOPiv	$Ni(OAc)_2 \cdot 4H_2O$	61[c]
10	DMA	NaOPiv	$Ni(OAc)_2 \cdot 4H_2O$	72[c, d]
11	**DMA**	NaOPiv	**$Ni(DME)Cl_2$**	**77[c, d, e]**
12	DMA	NaOPiv	$Ni(DME)Cl_2$	---[c,d,e,f]
13	DMA	NaOPiv	---	---[d,e]

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), [Ni] (10 mol %), Additive (0.50 mmol), nBu_4NBF_4 (0.50 mmol), Solvent (2.5 mL), CCE = 8 mA, 10 h, N_2, RVC(+)/Ni foam(-). [b] under air. [c] [Ni] (20 mol %). [d] NaOPiv (0.25 mmol). [e] DMA (3.0 mL). [f] no current. DMA = *N*,*N*-Dimethylacetamide, GVL = γ-Valerolactone, NMP = *N*-Methyl-2-pyrrolidinone, DMF = *N*,*N*-Dimethylformamide.

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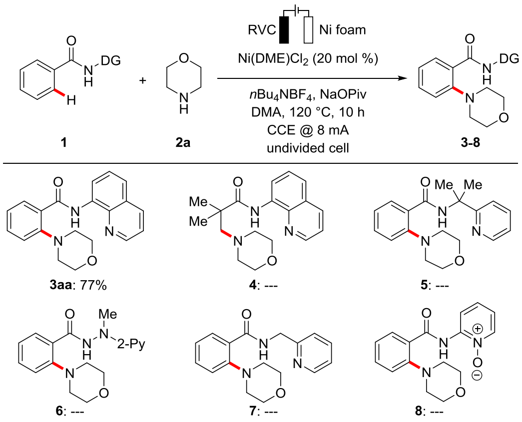
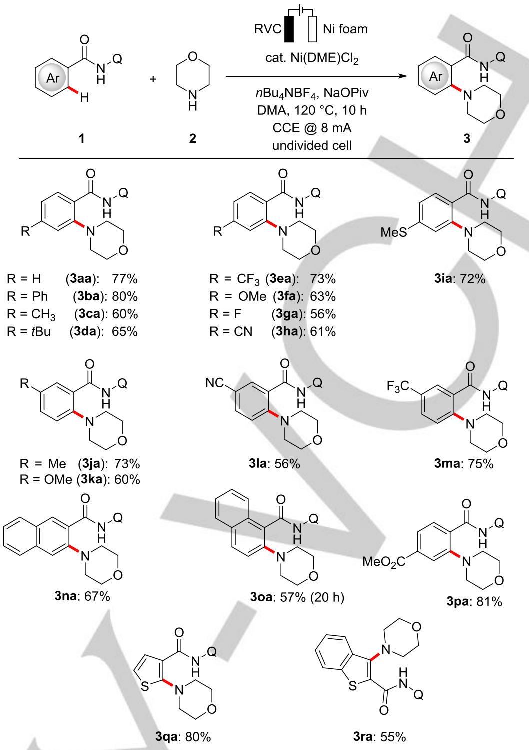
With the catalytic conditions being optimized, we next probed the effect exerted by the *N*-substituent of benzamides **1** (Scheme 1). Hence, various *N*,*N*-coordination modes (**4**–**7**), and an *N*,*O*-bidentate chelation (**8**) met with limited success, clearly contrasting with a cobalt catalysis manifold.[10c]



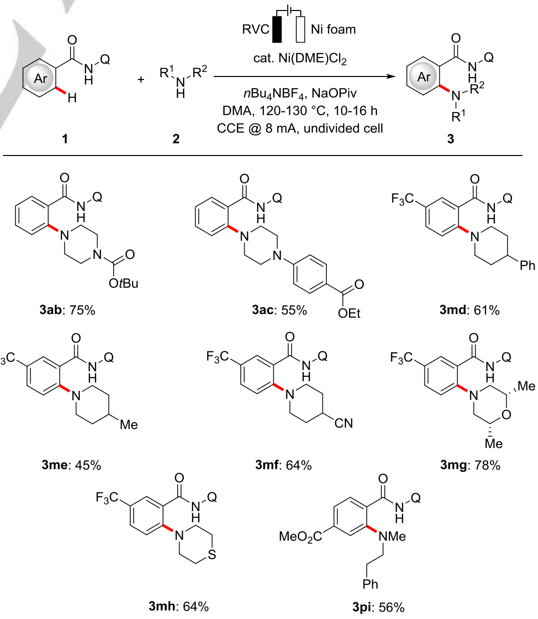
Scheme 1. Influence of *N*-substituents on benzamides **1**.

After having established an efficient nickel-catalyzed electroamination, we tested its robustness with different benzamides **1** (Scheme 2). Thus, diversely decorated arenes **1** were smoothly converted, thereby fully tolerating valuable functional groups, such as halo, sulfide or ester substituents. Intramolecular competition experiments with *meta*-substituted substrates **1j**–**m** were fully governed by steric interactions, exclusively delivering the products **3ja**–**3ma**. The versatile nickel catalyst was not limited to arene diversification. Indeed, the heteroarenes **1q** and **1r** were identified as amenable substrates likewise.



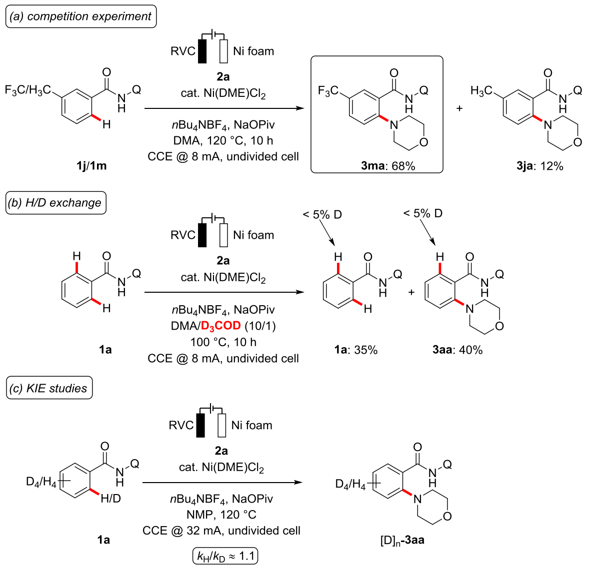
Scheme 2. Nickel-catalyzed electrochemical C–H amination of arenes **1**.

Moreover, the nickel catalyst enabled electrochemical C–H aminations with differently substituted secondary amines (Scheme 3).[17] Thereby, useful functional groups were chemo-selectively tolerated, featuring among others ester and cyano substituents. It is noteworthy that thiazine derivatives and even more challenging acyclic secondary amine **2i** could be employed as well.



Scheme 3. Nickel-catalyzed electrochemical C–H amination with amines **2**.

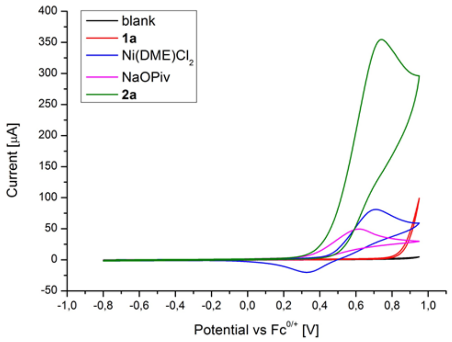
Given the versatility of the nickel-electrocatalyzed C–H amination under redox-mediator-free conditions, we felt intrigued to interrogating its modus operandi. To this end, we first conducted intermolecular competition experiments (Scheme 4a). In contrast to all previously reported electrooxidative C–H activations with palladium,[5] rhodium,[6] ruthenium,[7] iridium,[8] or cobalt catalysts,[9,10] the more electron-deficient arenes reacted faster here. These findings are indicative of a concerted-metalation-deprotonation mechanism[18] being operative in the C–H metalation. In good agreement with this observation, we, second, did not find H/D scrambling when using D_3COD as the cosolvents (Scheme 4b). Third, a kinetic isotope effect of k_H/k_D = 1.1 by independent experiments was suggestive of a fast[19] C–H scission (Scheme 4c).



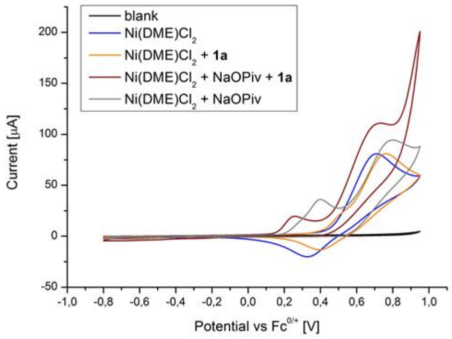
Scheme 4. Mechanistic studies on nickel-electrocatalytic C–H amination.

Finally, we conducted detailed studies by means of cyclic voltammetry (Figure 2a-c, and Figures S–7-S–12 in the Supporting Information).[16] Hence, the electrode potential for the nickel(II/III) event was found to be strongly influenced by the addition of both the substrate and NaOPiv to be thus observed at E_p = +0.26 V *vs.* $Fc^{+/0}$ (orange) (Figure 2a and 2b). Notably, at the elevated temperature at which catalysis occurred the reversible oxidation wave was significantly shifted to E_p = -0.18 V *vs.* $Fc^{+/0}$ (purple), which can be rationalized by the formation of cyclometalated nickel(III) catalyst. Interestingly, we furthermore observed an additional reversible oxidation wave at E_p = +0.49 V *vs.* $Fc^{+/0}$, which is furthermore indicative of an oxidation to a nickel(IV)[20] species.

(a) components of the reaction mixture



(b) at 25 °C



(c) after heating at 120 °C

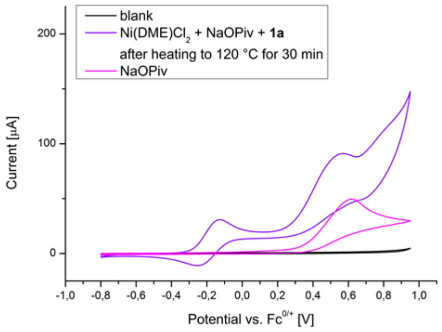
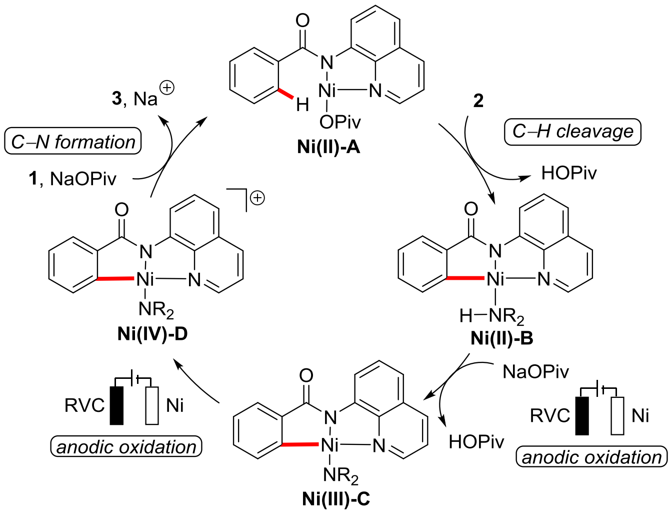


Figure 2. CV data (DMA, 0.05 M $[nBu_4N][BF_4]$, 100 mV/s) for a) the individual components of the catalytic manifold. b) $Ni(DME)Cl_2$ with the individual components of the catalysis. c) $Ni(DME)Cl_2$, NaOPiv and **1a** after preheating at 120 °C for 30 min.

Based on our mechanistic studies, we propose a plausible catalytic cycle to initiate by a rate-determining carboxylate-assisted C–H nickelation to deliver intermediate **Ni(II)-B** (Scheme 5). Thereafter, deprotonation of the coordinated amine and anodic oxidation generates the nickel(III)amide complex **Ni(III)-C**. In consideration of our cyclic voltammetry studies, electrochemical single electron transfer (SET) finally sets the stage for an oxidation-induced reductive elimination from intermediate **Ni(IV)-D**, thereby yielding the desired product **3**, while regenerating the catalytically competent complex **Ni(II)-A**.



Scheme 5. Plausible catalytic cycle.

In conclusion, we have reported on the first nickel-catalyzed electrooxidative C−H amination. The carboxylate-enabled nickel-electrocatalysis occurred with broad substrate scope and high levels of chemo- and position-selectivity. In contrast to all previous metal-catalyzed electrochemical C−H activations, the nickel electro-regime proved particularly potent in the C−H nitrogenation of electron-deficient arenes. Detailed mechanistic studies provided strong support for a fast C−H nickelation and an oxidation-induced reductive elimination at nickel(IV).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Electrochemistry • C−H activation • Mechanism • Nickel catalysis • Selectivity • Nickel(IV)

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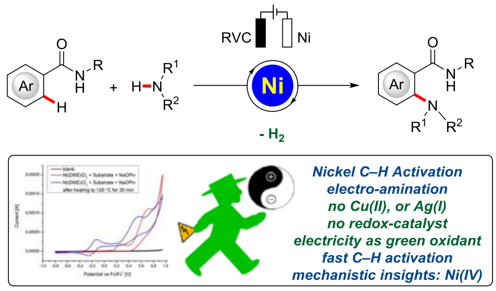
COMMUNICATION



Nickel C–H Activation
electro-amination
no Cu(II), or Ag(I)
no redox-catalyst
electricity as green oxidant
fast C–H activation
mechanistic insights: Ni(IV)

II…III…IV: Nickel-catalyzed C–H aminations proved viable with electricity as the sole oxidant by fast C–H cleavage involving nickel(IV) species.

*Shou-Kun Zhang, Ramesh C. Samanta, Nicolas Sauermann and Lutz Ackermann**

Page No. – Page No.

Nickel-Catalyzed Electrooxidative C–H Amination: Support for Nickel(IV)