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Electrochemistry *Hot Paper*

Electroreductive Synthesis of Nickel(0) Complexes**

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Abstract: Over the last fifty years, the use of nickel catalysts for facilitating organic transformations has skyrocketed. Nickel(0) sources act as useful precatalysts because they can enter a catalytic cycle through ligand exchange, without needing to undergo additional elementary steps. However, most Ni(0) precatalysts are synthesized with stoichiometric aluminum–hydride reductants, pyrophoric reagents that are not atom-economical and must be used at cryogenic temperatures. Here, we demonstrate that Ni(II) salts can be reduced on preparative scale using electrolysis to yield a variety of Ni(0) and Ni(II) complexes that are widely used as precatalysts in organic synthesis, including bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)$_2$]. This method overcomes the reproducibility issues of previously reported methods by standardizing the procedure, such that it can be performed anywhere in a robust manner. It can be transitioned to large scale through an electrochemical recirculating flow process and extended to an in situ reduction protocol to generate catalytic amounts of Ni(0) for organic transformations. We anticipate that this work will accelerate adoption of preparative electrochemistry for the synthesis of low-valent organometallic complexes in academia and industry.

Nickel has become an indispensable metal across many areas of organic synthesis, not only because of its abundance compared to precious metals like palladium, but also because of its unique reactivity and coordination patterns.[1b,c,2a,b] Low-valent nickel plays a crucial role as a precatalyst, reactive intermediate, and organometallic precursor because it can engage in reactivity through simple ligand exchange, without needing to be activated first.[1a,3,4a,c–f] As such, low-valent nickel precatalysts are an indispensable tool for early reaction screening and have been used in industrial processes[5] like the du Pont adiponitrile process[6] and ethylene polymerization.[7] Among the most common forms of low-valent nickel, Ni(COD)$_2$ (**1**), which was first described by Wilke in 1960,[8a] remains the most popular despite the recent uptick in reports of air-stable variants by our lab as well as the Cornella and Montgomery groups (Scheme 1A).[1d,9,10] While a number of methods for the preparation of Ni(COD)$_2$ have been reported,[8d–f] the most common route involves excess diisobutylaluminum hydride (DIBAL–H), a pyrophoric chemical reductant that must be used at cryogenic temperatures (Scheme 1B, 1).[1d,8b,c] A more efficient and greener way to prepare Ni(COD)$_2$ from Ni(II) salts would be through electrochemical reduction.[11] In this regime, electrons supplied at the cathode reduce Ni(II) to Ni(0), which is then trapped by 1,5-cyclooctadiene ligands, and a counter-oxidation at the anode leads to sacrificial salts. Lehmkuhl and Leuchte described the electrochemical reduction of nickel(II) salts to produce Ni(COD)$_2$ (Scheme 1B, 2).[12] However, this prior methodology suffers from a variety of drawbacks including reproducibility concerns. Herein, a standardized electrochemical procedure for the synthesis of nickel precatalysts from Ni(II) salts is disclosed (Scheme 1C). The results demonstrate how a variety of Ni(0) precatalysts can be safely and efficiently synthesized on preparative scales through electrochemistry without solvent-quantities of pyridine. The reductive platform can be modified to access a variety of important air-stable Ni(0)

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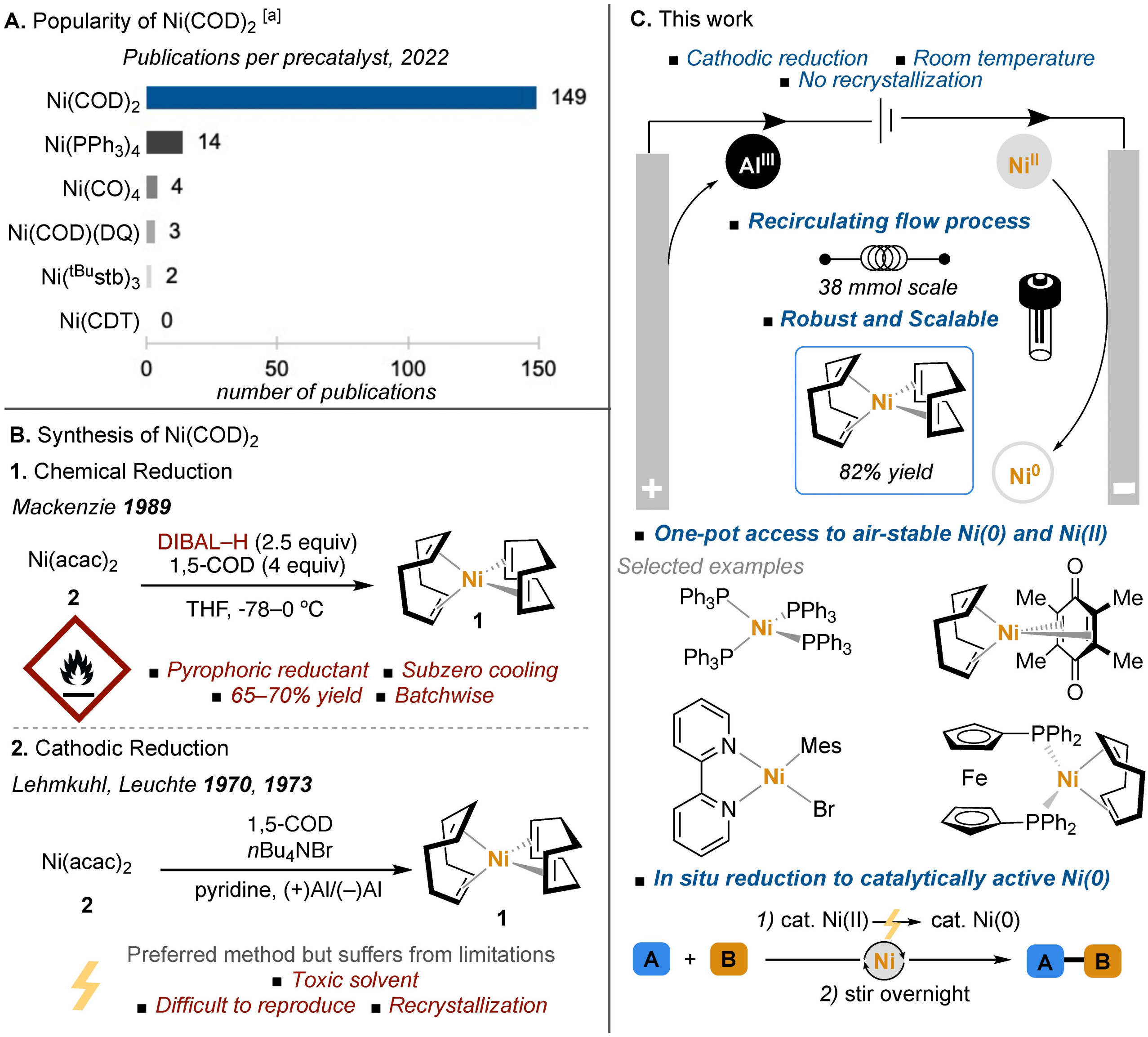
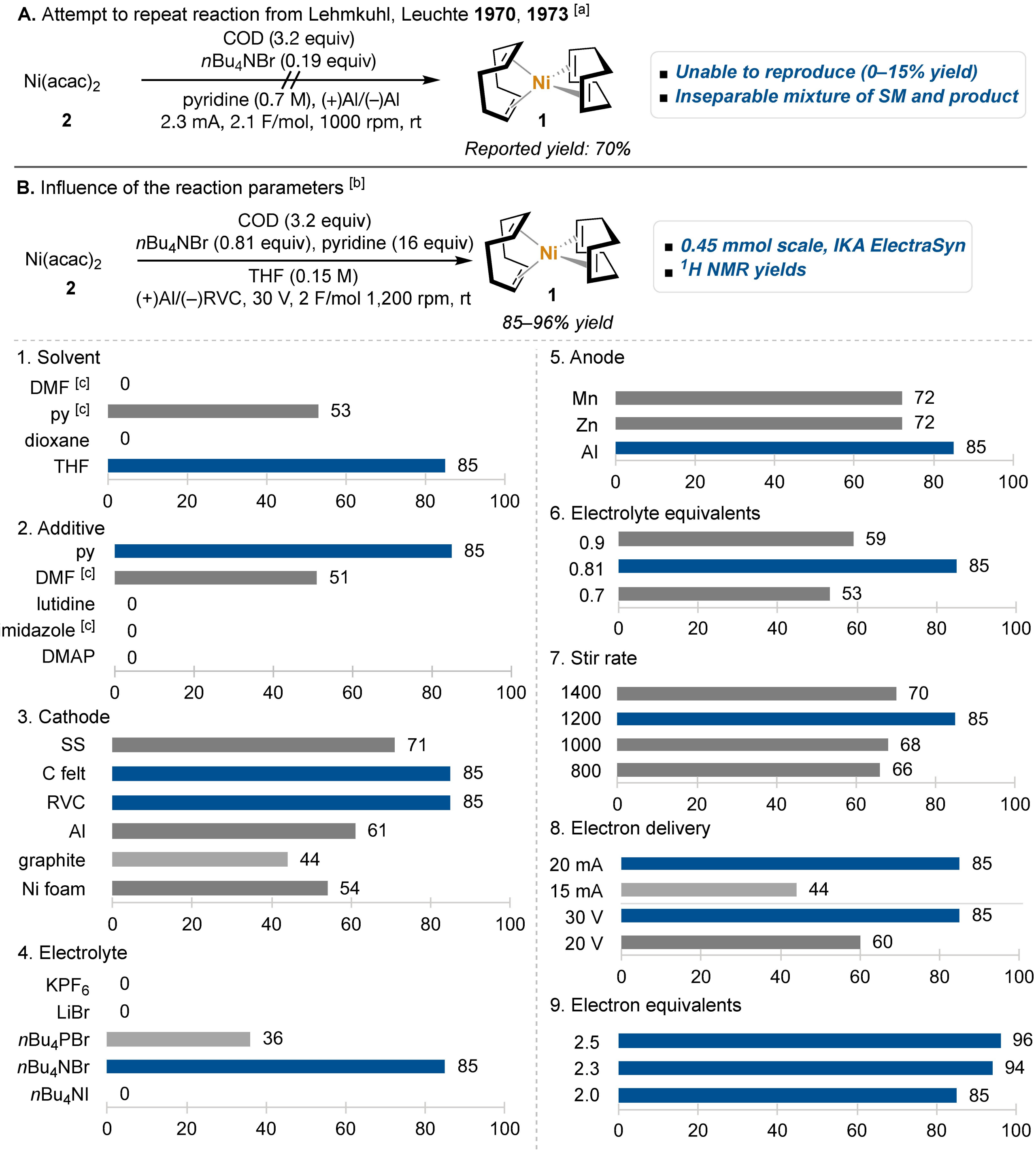


Scheme 1. Relevance, precedents, and synopsis of this work. [a] Information on construction of graph in Supporting Information p. S31.

and Ni(II) precatalysts and can also be used to generate catalytic amounts of nickel to initiate catalytic organic transformations.

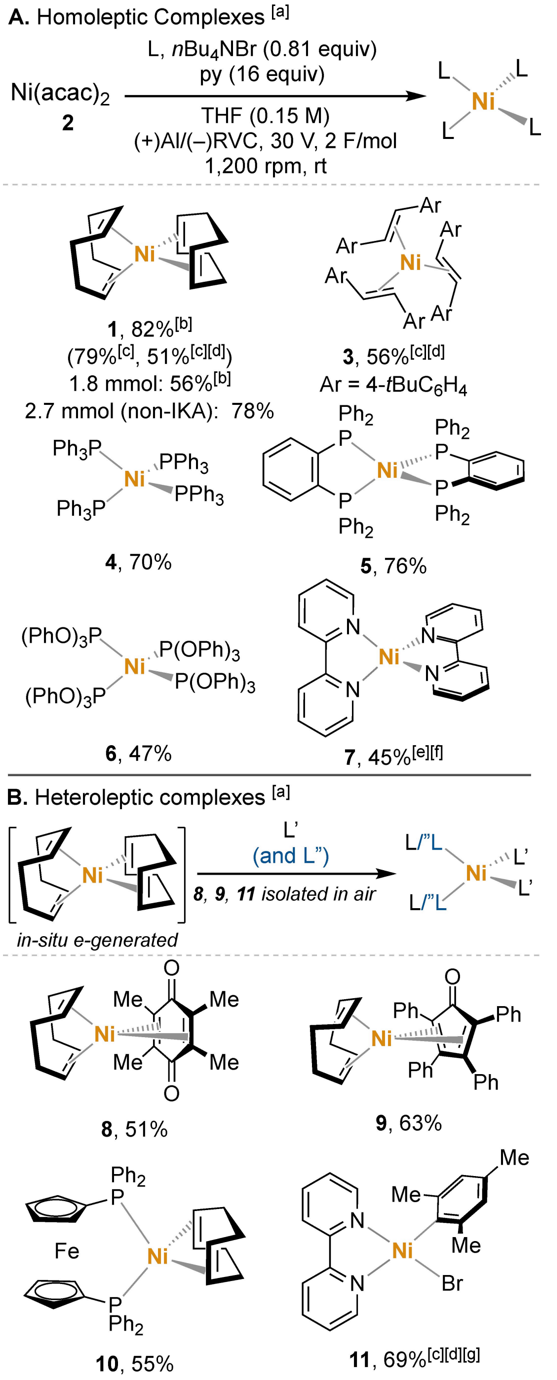
To begin this study, conditions from two reports by Lehmkuhl and Leuchte for the electrochemical synthesis of $Ni(COD)_2$ were repeated in several laboratories involved in this study (Scheme 2A).[12] Despite numerous attempts, only up to 15 % of the desired product could be obtained as an inseparable mixture of starting material and product.[13] It is common for older reports of electrochemical reactions to be irreproducible today because of missing experimental details, such as electrode size, distance between electrodes, flask dimensions, and stir rate. Even when such details are available, the need for custom glassware to repeat a known experiment limits ease of implementation, or the glassware dimensions may be larger or smaller than desired. Fortunately, the IKA ElectraSyn 2.0 allows modern-day chemists to overcome such limitations by standardizing the electrochemical setup, facilitating the development of reproducible procedures. Thus, all batchwise experiments described in this report were performed using the ElectraSyn 2.0, unless otherwise stated. Reaction optimization was undertaken with the goal of developing a reproducible and scalable procedure to access Ni(0) precatalysts. After extensive screening, reproducible reaction conditions that avoided solvent levels of pyridine were identified that led to 85–96 % ^{1}H NMR yield of $Ni(COD)_2$ (Scheme 2B). To delineate the reaction's sensitivity to each variable, a systematic evaluation of the reaction parameters relative to the optimal conditions was performed. One of the primary goals of this work was to avoid using pyridine as solvent. Based on reported cyclic voltammetry data of related systems, we imagined that a safer, moderately coordinating solvent could be combined with a highly coordinating additive that would lower the reduction potential of the resulting nickel species.[14–17] As such, THF was identified as a viable



Scheme 2. Optimization of reaction conditions. [a] Reaction details in Supporting Information. [b] Reactions performed on 0.45 mmol scale. Yields determined by ^{1}H NMR analysis using ferrocene as internal standard. [c] Constant current of 20 mA applied.

solvent.[18] Evaluation of various coordinating additives led to the conclusion that pyridine remained best.[14] Other notable findings include that ammonium or phosphonium bromides were the only classes of successful electrolyte for the transformation and that the reaction was extremely sensitive to electrolyte equivalents and stir rate. The reaction was found to be sensitive to water[19] and could be performed with similar results at a constant potential of 30 V or a constant current of 20 mA, but 30 V was found to be more robust when pyridine was used as additive.[20]

The electrochemical method resulted in high isolated yield of Ni(COD)$_2$ under constant current or constant potential (Scheme 3A). The procedure was independently reproduced by three laboratories involved in this study in 85, 84, and 71 % ^{1}H NMR yield. To avoid pyridine altogether, DMF could be used as an alternative additive,

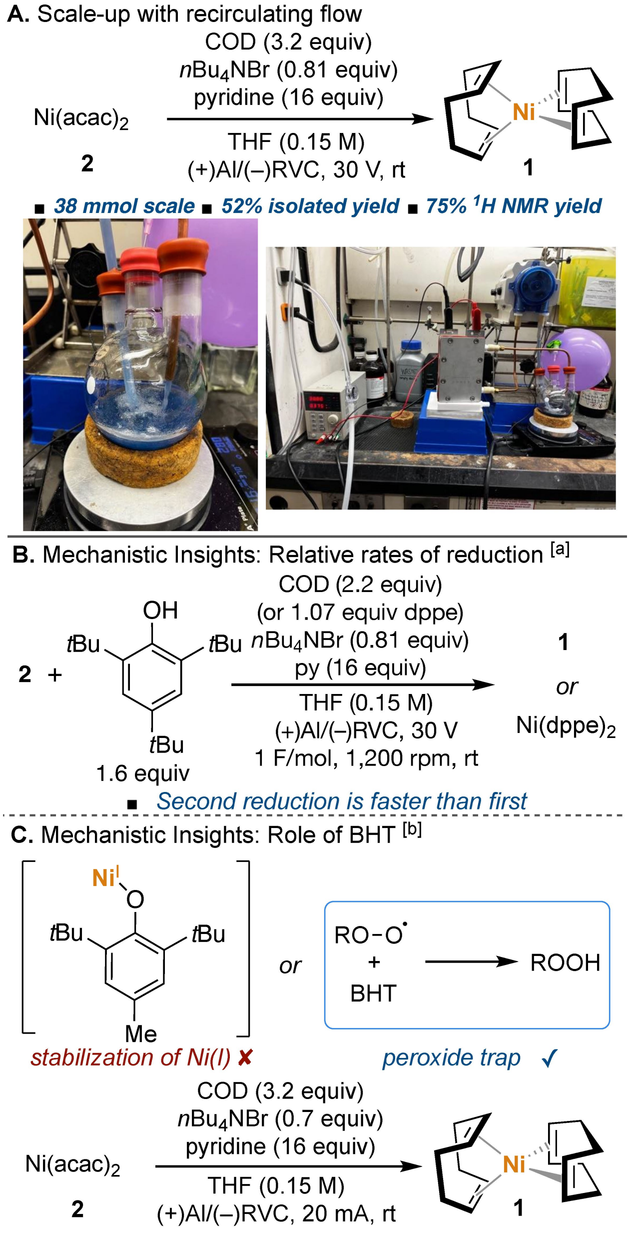


Scheme 3. Substrate scope. [a] Reactions performed on 0.45 mmol scale. Percentages represent isolated yields unless otherwise stated. Equivalents of L vary and can be found in Supporting Information. [b] 2.2 F/mol. [c] 20 mA instead of 30 V. [d] DMF instead of py. [e] 12 mA constant current. [f] Yield represents ^{1}H NMR yield according to ferrocene internal standard. [g] 1 equiv. bipyridine added prior to electrolysis.

albeit with a diminished yield of 51 %.[21] The reaction could also be easily translated to non-ElectraSyn batch reactors, giving 78 % yield on 2.7 mmol scale. Next, the developed reaction conditions were applied to the synthesis of other nickel complexes (Scheme 3). The majority of nickel complexes and precatalysts examined are typically either made via reduction of Ni(II) using pyrophoric organometallic reagents like in the case of Ni(COD)$_2$, or in an inefficient, multi-step fashion from Ni(COD)$_2$ or *trans*,*trans*,*trans*-(1,5,9-cyclododecatriene)nickel(0) [Ni(CDT)].[4b,9c,b,e, 22,23] Using our optimized method, 16-electron nickel-olefin complex Ni-(^{tBu}stb)$_3$ (**3**) was synthesized in moderate yield. Complex **3** is an air-stable Ni(0) complex of growing importance that is currently made from nickel(II) acetylacetonate [Ni(acac)$_2$] and AlEt$_3$.[9d] Monophosphine, phosphite, and bisphosphine were tolerated under the reaction conditions to afford Ni(PPh$_3$)$_4$ (**4**), Ni(dppbz)$_2$ (dppbz = 1,2-bis(diphenylphosphino)benzene) (**5**), and Ni[P(OPh)$_3$]$_4$ (**6**) in moderate to high yields.[24] Bipyridine was also compatible and led to 45 % ^{1}H NMR yield of the unstable Ni(bipy)$_2$ (**7**). In most cases, the remaining mass balance was due to material lost in the mother liquor, formation of nickel black during electrolysis, or decomposition during isolation (for very sensitive compounds). Engle recently reported a family of air-stable Ni(COD)(L) complexes with promising reactivity.[9e] However, a major limitation to their widespread use is their synthesis; pure Ni(COD)$_2$ is an essential starting material or intermediate. While the dienyl supporting ligands were not tolerated under electrochemical conditions, we found that by simply removing solvent after electrolysis and charging the proper ligand and solvent, Ni(COD)(DQ) (DQ = duroquinone) (**8**) and Ni(COD)-(CPD^H) (CPD^H = tetraphenylcyclopentadienone) (**9**) could be isolated in air in moderate yields of 51 % and 63 %, respectively (Scheme 3B). This simple, inexpensive route could expedite commercialization of the precatalyst toolkit. Precatalysts Ni(COD)(DPPF) (DPPF = 1,1′-bis(diphenylphosphino)ferrocene) (**10**) and Ni(bipy)-(Mes)Br (Mes = mesityl) (**11**) could also be prepared in moderate yields by simply adding the appropriate ligands to the crude product mixture after electrolysis.

To demonstrate the viability of the reaction on large scale, a recirculating flow process was developed (Scheme 4A). An advantage of electrochemistry is the ease with which reactions developed in sub-mmol quantities can be scaled.[25,26] In accordance, our first attempt of the 37.5 mmol scale synthesis of Ni(COD)$_2$ using electrochemical recirculating flow resulted in a 52 % isolated yield of Ni(COD)$_2$ (75 % yield by ^{1}H NMR).

During evaluation of the substrate scope, a few mechanistic observations were made. First, attempts to make the Ni(I) phenolate complexes recently reported by Morandi and co-workers by applying 1 F/mol resulted in the formation of the corresponding Ni(0) complex, depending on the supporting ligand used (Scheme 4B).[27] This result indicates that as soon Ni(II) is reduced to Ni(I), it undergoes a second reduction faster than it can diffuse away from the cathode. Second, during the screening process, yield discrepancies were observed between different bottles of uninhibited THF (Scheme 4C). This issue was resolved by using THF supplied with the radical inhibitor BHT (butylated hydroxytoluene). We hypothesize that the inhibitor prevents yield variability by maintaining low peroxide levels in the solvent during long-term storage.[28] Entries 1–4 in Scheme 4C.2 demon-



Entry	BHT source	yield (%)
1	commercial THF with BHT (batch A)*	79
2	THF without BHT (batch B)	49
3	THF without BHT (batch C)	52
4	THF without BHT (batch D)	70
5	(batch D), 0.19 mol% BHT added	71
6	(batch A), 10 mol% BHT added	37

*Commercial THF with 250 ppm BHT correspond to 0.185 mol%

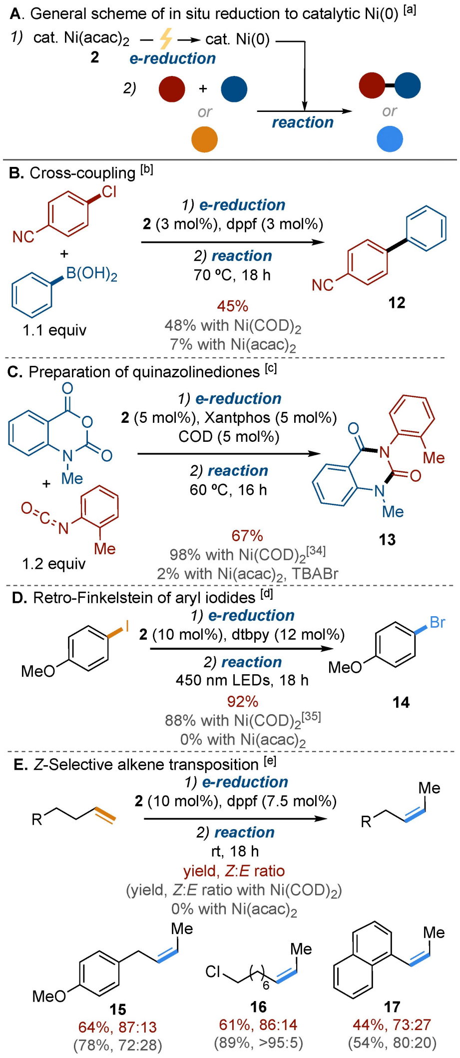
- *Variable peroxide concentration in THF w/o BHT →inconsistent yields*

Scheme 4. Scale-up in flow, and mechanistic findings. [a] Reactions run on 0.30 mmol scale. [b] Reactions run on 0.45 mmol scale. Yields represent ^{1}H NMR yields relative to ferrocene internal standard.

strate the variability in yield in THF bottles that are supplied without BHT. Entry 5 shows that BHT must be present from the source to keep peroxide levels low, and entry 6 rules out that BHT is stabilizing Ni(I) intermediates because it is detrimental to the reaction in higher quantities. Thus, variation in yield between BHT-free THF batches (entries 2–4) was attributed to variation in peroxide content.

We next wondered whether the electrochemical reduction method could be used to generate reactive Ni(0) from a dormant Ni(II) species and initiate a catalytic cycle (Scheme 5A). In situ reduction using substoichiometric organic reductants is common for generating catalytic quantities of low-valent nickel,[2c,29] but electrochemical reduction for this purpose has been limited to the polymerization or oligomerization of olefins or electroreductive processes that require reduction of nickel for catalytic turnover.[12e,30–32] One of the most enabling uses of in situ reduction would be nickel-catalyzed cross-coupling. With slight modifications from a previously described Suzuki–Miyaura coupling that requires Ni(0) precatalyst, a catalytic amount of Ni(acac)$_2$ was electrochemically reduced in the presence of electrolyte and ligand (Scheme 5B).[33] After electrolysis, aryl chloride, aryl boronic acid, and base were added, and the reaction mixture was heated overnight to afford 45 % of biaryl **12**. A similar procedure was followed to prepare quinazolinedione **13** from an isocyanate derivative and isatoic anhydride in 67 % yield (Scheme 5C).[34] Taking advantage of the presence of electrolyte, a photochemical retro-Finkelstein of aryl iodides could also be performed (Scheme 5D).[35] Notably, in situ reduction resulted in a highly active catalyst, as irradiating at room temperature gave a slightly higher yield of aryl bromide **14** than the reported procedure, which was performed at 50 °C with Ni(COD)$_2$. Lastly, the *Z*-selective olefin transposition of terminal olefins was undertaken (Scheme 5E).[36] Using the in situ reduction protocol, an alkenyl chloride, allyl arene, and homoallyl arene underwent the *Z*-selective alkene transposition in moderate yields and selectivities (**15**–**17**). All the selected examples were unsuccessful without electrolysis.

Overall, an electrochemical method for the synthesis of Ni(COD)$_2$ and a variety of useful Ni(0) precatalysts was developed. Because this method replaces stoichiometric pyrophoric reagents with a simple cathodic reduction either using an ElectraSyn 2.0 instrument or a recirculating flow setup, it can be performed at ambient temperatures and large scales, making it robust and widely reproducible. In addition, it avoids the use of solvent-quantities of pyridine and can be readily adapted to the synthesis of multiple classes of nickel complexes. For these reasons, we expect that this approach toward the preparation of low-valent nickel will find rapid adoption in industry and academia. These findings may also inspire new electrochemical methodologies for the synthesis of precatalysts of other metals, such as cobalt, manganese, and iron.



Scheme 5. In situ reduction. [a] Yields in red represent isolated yields. Yields in grey did not include electrolyte unless otherwise noted and were not electrolyzed. CH_2Br_2 internal standard was used to calculate ^1H NMR yields written in grey. Yields in grey with references in brackets are according to literature. [b] Before electrolysis, **2** (0.009 mmol, 3 mol%), dppf (0.009 mmol, 3 mol%), nBu$_4$Br (0.03 mmol, 10 mol%), THF (0.17 M). Electrolysis using (+)Al/(−)RVC, 20 mA, 2 F/mol **2**, 1200 rpm. After electrolysis, addition of 4-chlorocyanobenzene (0.30 mmol, 1.0 equiv), phenylboronic acid (0.33 mmol, 1.1 equiv), K_3PO_4 (0.90 mmol, 3.0 equiv), and heating at 70 °C for 18 h. [c] Before electrolysis, **2** (0.11 mmol, 5 mol%), Xantphos (0.11 mmol, 5 mol%), COD, (0.11 mmol, 5 mol%), and nBu$_4$Br (0.089 mmol, 4 mol%), pyridine (15.5 mmol, 7.0 equiv), DMF (0.32 M). Electrolysis using (+)Al/(−)RVC, 20 mA, 2 F/mol **2**, 1200 rpm. After electrolysis, addition of *N*-methylisatoic anhydride (2.2 mmol, 1.0 equiv), *o*-tolyl isocyanate (2.66 mmol, 1.2 equiv), and heating at 60 °C for 16 h. [d] Before electrolysis, **2** (0.03 mmol, 10 mol%), 4,4′-di-tert-butyl-2,2′-bipyridine (0.036 mmol, 12 mol%), nBu$_4$Br (1.50 mmol, 5.0 equiv), THF (0.10 M). Electrolysis using (+)Al/(−)carbon felt, 20 mA, 2 F/mol **2**, 1200 rpm. After electrolysis, addition of 1-iodo-4-methoxybenzene (0.30 mmol, 1.0 equiv), and irradiation at 467 nM at rt for 18 h. [e] Before electrolysis, **2** (0.03 mmol, 10 mol%), dppf (0.023 mmol, 7.5 mol%), nBu$_4$I (0.150 mmol, 0.5 equiv), 1-iodo-4(trifluoromethyl)benzene (0.150 mmol, 0.5 equiv), alkene (0.300 mmol, 1.0 equiv), DMF (0.10 M). Electrolysis using (+)Al/(−)carbon felt, 20 mA, 2 F/mol **2**, 1200 rpm. After electrolysis, stirring at rt for 18 h.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Electrochemistry · Flow Chemistry · Green Chemistry · Nickel Catalysis · Precatalyst

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[18] THF was employed as solvent for the synthesis of $Ni(PPh_3)_4$ in ref. 12d.

[19] See Supporting Information Table S9.

[20] See Supporting Information Figures S17 and S18.

[21] DMF was employed as solvent for the synthesis of $Ni(COT)_2$ in ref. 12d.

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Communications

Electrochemistry

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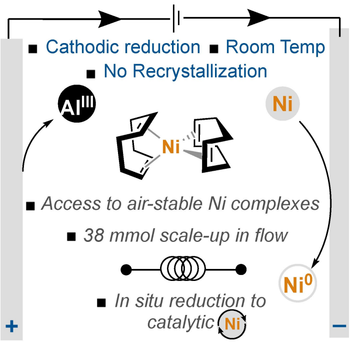
Electroreductive Synthesis of Nickel(0) Complexes



An electrochemical reduction of Ni(II) salts to make Ni(COD)$_2$ on preparative scales is reported. The method was extended to other useful precatalyst complexes such as Ni(COD)(DQ), Ni(^{tBu}stb)$_3$, Ni(COD)(DPPF), and Ni(PPh$_3$)$_4$. A 38 mmol scale-up was demonstrated with recirculating flow, and the electrochemical platform could be used to reduce a catalytic amount of Ni(II) to initiate a nickel(0)-catalyzed organic transformation.