Merging Electrolysis and Nickel Catalysis in Redox Neutral Cross-Coupling Reactions: Experiment and Computation for Electrochemically Induced C–P and C–Se Bonds Formation

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We have achieved a nickel-catalyzed cross-coupling reaction via concerted paired electrolysis under mild reaction conditions. In this electrochemical transformation, the anodic oxidation of NiII to NiIII and cathodic reduction of NiI to Ni0 occurred simultaneously, resulting in an economical and sustainable cross-coupling protocol. Moreover, we performed mechanistic investigations, achieved by experiments and density functional theory (DFT) calculations for different C–heteroatom bond formations to reveal the catalytic cycle in more detail.

Keywords: nickel catalysis, paired electrolysis, redox neutral, cross-coupling, C–P bond formation, C–Se bond formation, aryl halides, DFT calculations

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Introduction

The development of green and sustainable synthetic methodologies to access structurally diverse organic compounds is a long-term aim for organic chemists. In this regard, organic electrochemistry has been developed as an attractive catalytic platform, making use of renewable electricity instead of employing stoichiometric oxidants or reductants.\(^1\)–\(^14\) Compared with other catalytic methods, electrolysis possesses many advantages, including energy economy, cost-efficiency, sustainability, high reactivity and chemoselectivity, mild reaction conditions, broad substrate scope, and scalability, making it a practical technique.\(^15\)–\(^33\) Despite these benefits, most electrochemical transformations only exploit one of the two half-reactions to afford the desired products, while the other side usually undergoes a redox process of solvent, electrolyte, or sacrificial electrodes (Scheme 1a and 1b).\(^6\) In contrast, paired electrolysis is a more attractive method in which the half-reactions at both anode and cathode contribute simultaneously to the formation of the desired products, thus improving the atom economy and energy efficiency of the catalytic process.\(^34\)–\(^43\)

Typically, there are three main types of paired electrolysis, namely, parallel-, sequential-, and convergent paired electrolysis. More recently, progress has been made in the “concerted paired electrolysis” via the combination of electrolysis and nickel catalysis.\(^44\)–\(^48\) In these approaches, both the anode and the cathode are used to modulate directly or indirectly the oxidation state of nickel (Ni) to facilitate the reductive elimination step and to regenerate the activated nickel species. Since organophosphorus compounds are essential chemicals that have many applications as pharmaceuticals, agrochemicals, ligands, and materials,\(^49\)–\(^54\) the conventional methods to access these compounds mainly focus on cross-coupling of aryl halides with H-phosphonates at high temperature.\(^55\)–\(^60\) Recently, milder catalytic protocols have been developed by the combination of photoredox and nickel dual catalysis.\(^61\),\(^62\) These methods use less abundant aryl iodides as substrates, more air-sensitive Ni\(^0\) complex, and more expensive photocatalysts elements such as Ir or Ru as catalysts. The electrochemical C–P bond formation via dehydrogenative C–H/P–H cross-coupling was realized recently.\(^63\)–\(^66\) As part of our continuing studies in the area of C–P bond formation and Ni\(^{III}\)-involved transformations,\(^67\)–\(^73\) we herein report a C–P and C–Se bonds formation via a strategy of merging electrolysis and nickel catalysis. In this transformation, electricity was applied to facilitate the generation of unstable Ni\(^{III}\) intermediate, which was prone to undergo reductive elimination, required in C–P and C–Se bonds formation. Alteration of the nickel (Ni\(^{II}\) to Ni\(^{III}\)) oxidation state significantly reduced the energy barrier of the reductive elimination reaction when compared with the Ni\(^{II}\) complex (Scheme 1c). Thus, similar to a paired electrolysis process, where two products or reactive intermediates are formed, both of the half-reactions participated in the generation of the reactive nickel species.

### Experimental Method

General procedure for the catalytic reactions: A dry 5 mL screw-cap tube, equipped with a Teflon-coated magnetic stirring bar was charged with aryl halide (0.2 mmol, 1 equiv., if solid), H-phosphonate (0.3 mmol, 1.5 equiv., if solid), nickel chloride dimethoxyethane (NiCl\(_2\)·dme) (4.4 mg, 0.02 mmol, 10 mol%); 2,2′-bipyridine (bpy) (3.1 mg, 0.02 mmol, 10 mol%), tripotassium phosphate (K\(_3\)PO\(_4\)) (84.9 mg, 0.4 mmol, 2 equiv.); and tetra-n-butylammonium bromide (Bu\(_4\)NBr) (257.9 mg, 0.8 mmol, half-reactions to afford the desired products, while the other side usually undergoes a redox process of solvent, electrolyte, or sacrificial electrodes (Scheme 1a and 1b).\(^6\) In contrast, paired electrolysis is a more attractive method in which the half-reactions at both anode and cathode contribute simultaneously to the formation of the desired products, thus improving the atom economy and energy efficiency of the catalytic process.\(^34\)–\(^43\)

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4 equiv.) in a glovebox. Anhydrous and degassed dimethylacetamide (DMA) (4.0 mL); aryl halide (0.2 mmol, 1 equiv., if liquid); H-phosphonates (0.3 mmol, 1.5 equiv., if liquid) were added via syringe. Then, the vial was capped with a Teflon lid equipped with graphite felt electrode (20 × 7 × 2 mm) as the anode and foamed nickel electrode (20 × 10 × 1 mm) as the cathode. Following the stirring of the reaction mixture, the solution was electrolyzed at a constant current of 2 mA at room temperature for 12 h. After completion of the reaction, the mixture was transferred to a 25 mL round-bottom flask via syringe, and electrodes were washed with ethyl acetate. The solution was diluted with H2O (10 mL) and EtOAc (10 mL). The two layers were separated, followed by extraction of the aqueous layer with EtOAc (3 × 20 mL). The collected organic layers were combined and concentrated using a rotary evaporator. The product was purified by flash column chromatography on silica gel 60 (particles: 230-400 mesh, Sigma-Aldrich, Al-Khobar, Saudi Arabia) using hexane/EtOAc as eluent. Experimental details and characterization methods are available in Supporting Information.

Results and Discussion

Reaction optimizations

We started our investigation by evaluating the cross-coupling of 4-bromobenzonitrile 1a and diphenylphosphine oxide 2a using NiCl2·dme as the catalyst, dtbbpy as the ligand, K2PO4 as the base, Bu4NBr as an electrolyte, in 4 mL DMA with graphite/nickel foam (GFE/FNE) electrodes under a constant current condition at room temperature. The desired product 3a was obtained in 30% yield, which indicated that this electro-assisted nickel-catalyzed phosphorylation of aryl halide under mild experimental condition is feasible (Table 1, entry 1). Since ligands typically play a critical role in cross-coupling reactions, we next screened several bidentate and tridentate ligands (entries 2–7). The use of L2 gave the best result, with an improvement to 72%. Utilizing different inorganic (Na2CO3) and organic (pyridine) bases decreased the yield (entries 8–9), and solvents such as dimethylformamide (DMF) or acetonitrile (CH2CN) also gave lower yield (entries 10–11). Current adjustment showed that higher current diminished the yield (entry 12), while lowering the current setting to 2 mA enhanced the yield to 78% (entry 13). Additionally, a series of electrolytes were tested (entries 14–17) in which Bu4NBr was found to be the best for this catalytic reaction. Reevaluation of DMF and CH2CN using Bu4NBr as electrolyte resulted in comparable yields (entries 18–19). The reaction was also conducted under air; however, only a 40% yield was obtained (entry 20). Control experiments demonstrated that the nickel catalyst, ligand, base, electrolyte, and electrolyte were all essential for the success and high efficiency of this transformation (entries 21–25). On the contrary, no observation of product generation was made when the reaction was conducted using a divided cell (entry 26), which demonstrated further the importance of the concerted anodic oxidation and cathodic reduction of the nickel complex (paired electrolysis) in the catalytic cycle.

Substrate scope

With the optimized reaction conditions in hand, the scope of this newly developed phosphorylation protocol was evaluated next, employing a wide variety of aryl halides, including aryl bromides, aryl iodides, and even aryl chlorides could be smoothly transformed to the corresponding phospho-derivative products in good to excellent yields (Table 2). Both electro-poor and electro-rich substrates could be applied to this protocol. For example, aryl substrates bearing cyano, methyl ester, and acyl groups reacted successfully to give the corresponding derivatives in good to high yields (3a–3e). In addition, a series of functional groups, including sulfone, trifluoromethyl, trifluoro-methoxy, fluoro, t-butyl, methoxy, methylthio, amide, and amine were tolerated, highlighting the chemoselectivity of this method (3f–3r). Ortho-, meta- and para-fluoro-substituted substrates all underwent this reaction in good yields, indicating that steric hindrance had a minimal effect on the transformation efficiency (3j–3l). Notably, unprotected free primary amine and boronic ester kept untouched, providing the opportunity for further functionalization of the generated products (3s and 3t). Moreover, the reaction could occur with selectivity between C–I bond with substrates bearing both chloride and iodide group (3u). Biphenyl aryl bromide and iodide, disubstituted aryl bromide, and bicyclic substrates, including phthalimide and naphthyl halides, could also be converted to the products in good to excellent yields (3v–3ab). Remarkably, heteroaryl halides containing quinoline, pyridine, and thiophene group all underwent a feasible reaction using this protocol (3ac–3af). Substrates derived from natural products such as probenecid, adamantane carboxylic acid, and cholestanol also reacted with diphenylphosphine oxide in good to high yields (3ag–3al). Less-reactive aryl chlorides were also suitable substrates (3a, 3c, 3e, 3g, and 3ab). More importantly, vinyl halides and some other important H–P sources, including dialkyl phosphonates, could be applied to this protocol with good to excellent efficiency (3aj–3ap).

Further, we observed that the steric properties of aryl bromides and iodides had a small influence on the efficiency of this transformation since ortho-substituted 3aq–3as also gave the corresponding products in good yields. However, for some substrate scope, 2 equivalents of aryl halides and 2 equivalents of organic base “Bu3N were used (footnotes b and c). Notably, this newly developed
cross-coupling could be extended readily to C-Se bond formation. Electro-poor, electro-rich, and even sterically hindered aryl halides could all participate in this catalytic system, giving the corresponding derivatives in moderate to excellent yields (Scheme 2a, 5a–5e). Additionally, we conducted a gram-scale reaction successfully using 1z (10 mmol) and 2a as reactants with this catalytic system, and the desired product 3z was obtained in 87% yield in only 3 h (Scheme 2b) demonstrating the practicability of our newly developed methodology.

Mechanistic studies

To shed more light on the mechanism of this transformation, a series of mechanistic studies were conducted. The cyclic voltammetry (CV) measurement of diphenylphosphine oxide 2a showed no apparent oxidation peak of 2a, indicating that the generation of phosphorus radical was not involved in the reaction (Scheme 2e). Besides, we prepared in-situ the Ar–NiII–Br complex via the reaction of Ni0(bpy) and aryl bromide (Scheme 2f, Condition C). The reversible peak at 0.41 V versus Ag/AgNO3 was

Table 1 | Optimization of the Ni Catalytic Reaction Conditions

| Entry | Ligand | Base | Electrolyte | Yield (%)a |
|-------|--------|------|-------------|------------|
| 1     | L1     | K3PO4| LiBr        | 30         |
| 2     | L2     | K3PO4| LiBr        | 71         |
| 3     | L3     | K3PO4| LiBr        | 23         |
| 4     | L4     | K3PO4| LiBr        | 35         |
| 5     | L5     | K3PO4| LiBr        | 56         |
| 6     | L6     | K3PO4| LiBr        | 12         |
| 7     | L7     | K3PO4| LiBr        | 8          |
| 8     | L2     | Na2CO3| LiBr       | 28         |
| 9     | L2     | Pyridine| LiBr     | 13         |
| 10a   | L2     | K3PO4| LiBr        | 35         |
| 11a   | L2     | K3PO4| LiBr        | 13         |
| 12a   | L2     | K3PO4| LiBr        | 31         |
| 13a   | L2     | K3PO4| LiBr        | 74         |
| 14a   | L2     | K3PO4| Nal         | 26         |
| 15a   | L2     | K3PO4| LiClO4      | 78         |
| 16a   | L2     | K3PO4| Bu4NPF6     | 87         |
| 17a   | L2     | K3PO4| Bu4NBr      | 89         |
| 18a   | L2     | K3PO4| Bu4NPF6     | 87         |
| 19a   | L2     | K3PO4| Bu4NPF6     | 83         |
| 20a   | L2     | K3PO4| Bu4NBr      | 40         |
| 21a   | L2     | K3PO4| LiBr        | 0          |
| 22a   | L2     | K3PO4| Bu4NBr      | 3          |
| 23a   | L2     | K3PO4| Bu4NBr      | 12         |
| 24a   | L2     | K3PO4| -           | 32         |
| 25a   | L2     | K3PO4| Bu4NBr      | 15         |
| 26a   | L2     | K3PO4| Bu4NBr      | 0, 0%      |

a Reaction conditions: 1a (0.2 mmol), 2a (0.3 mmol), NiCl2·dme (0.02 mmol), ligand (0.02 mmol), base (2 equiv.), and electrolyte (4 equiv.) in 4.0 mL DMA at room temperature for 12 h. I = 4 mA. GFE = graphite felt electrode, FNE = foamed nickel electrode. GC yield using decane as internal standard. DMF as solvent. CH3CN as solvent. I = 6 mA. I = 2 mA. Under air condition. No NiCl2·dme. No electricity. 'Divided cell, all reagents in the anodic or cathodic chamber, only solvent and electrolyte in the other chamber. 'Divided cell, all reagents in both chambers.

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Table 2 | Scope of Substrates

| Scope of Substrates | Reaction conditions: aryl halide \(1\) (0.2 mmol), H-phosphonates \(2\) (0.3 mmol), NiCl\(_2\)-dme (0.02 mmol), ligand (0.02 mmol), K\(_3\)PO\(_4\) (2 equiv.), \(\text{Bu}_4\text{NBr}\) (4 equiv.) in 4.0 mL DMA at room temperature for 12 h, \(i = 2\) mA, \(j = 1\) mA cm\(^{-2}\), \(t, 12\) h.

| Aryl halide \(1\) | H-phosphonates \(2\) | Product \(3\) |
|------------------|------------------|--------------|
| \(X = \text{Br}\) | \(X = \text{Cl}\) | \(X = \text{I}\) |
| 3a | \(X = \text{Br}\), 80% | \(X = \text{Cl}\), 63% |
| 3b | \(X = \text{Br}\), 56% | \(X = \text{Cl}\), 50% |
| 3c | \(X = \text{Br}\), 82% | \(X = \text{Cl}\), 63% |
| 3d | \(X = \text{Br}\), 89% | \(X = \text{Cl}\), 63% |
| 3e | \(X = \text{Br}\), 70% | \(X = \text{Cl}\), 63% |
| 3f | \(X = \text{Br}\), 73% |
| \(X = \text{Br}\) | \(X = \text{Cl}\) | \(X = \text{I}\) |
| 3g | \(X = \text{Br}\), 80% | \(X = \text{Cl}\), 40% |
| 3h | \(X = \text{Br}\), 72% | \(X = \text{Cl}\), 65% |
| 3i | \(X = \text{Br}\), 56% | \(X = \text{Cl}\), 70% |
| 3j | \(X = \text{Br}\), 74% |
| 3k | \(X = \text{Br}\), 76% |
| 3l | \(X = \text{I}\), 66% |

| Aryl halide \(1\) | H-phosphonates \(2\) | Product \(3\) |
|------------------|------------------|--------------|
| \(X = \text{Br}\) | \(X = \text{Cl}\) | \(X = \text{I}\) |
| 3m | \(X = \text{Br}\), 87% | \(X = \text{Cl}\), 66% |
| 3n | \(X = \text{Br}\), 87% | \(X = \text{Cl}\), 66% |
| 3o | \(X = \text{Br}\), 63% | \(X = \text{Cl}\), 70% |
| 3p | \(X = \text{Br}\), 69% | \(X = \text{Cl}\), 70% |
| 3q | \(X = \text{Br}\), 61% |
| 3r | \(X = \text{I}\), 72% |

| Aryl halide \(1\) | H-phosphonates \(2\) | Product \(3\) |
|------------------|------------------|--------------|
| \(X = \text{Br}\) | \(X = \text{Cl}\) | \(X = \text{I}\) |
| 3s | \(X = \text{Br}\), 65% | \(X = \text{Cl}\), 66% |
| 3t | \(X = \text{Br}\), 66% | \(X = \text{Cl}\), 66% |
| 3u | \(X = \text{Br}\), 65% | \(X = \text{Cl}\), 66% |
| 3v | \(X = \text{Br}\), 65% | \(X = \text{Cl}\), 66% |
| 3w | \(X = \text{Br}\), 76% |
| 3x | \(X = \text{Br}\), 54% |
| 3y | \(X = \text{Br}\), 46% |

| Aryl halide \(1\) | H-phosphonates \(2\) | Product \(3\) |
|------------------|------------------|--------------|
| \(X = \text{Br}\) | \(X = \text{Cl}\) | \(X = \text{I}\) |
| 3z | \(X = \text{Br}\), 96% |
| 3aa | \(X = \text{Br}\), 72% |
| 3ab | \(X = \text{Br}\), 64% | \(X = \text{Cl}\), 64% |
| 3ac | \(X = \text{Br}\), 63% | \(X = \text{Cl}\), 64% |
| 3ad | \(X = \text{I}\), 50% |
| 3ae | \(X = \text{I}\), 63% |
| 3af | \(X = \text{Br}\), 40% |

| Aryl halide \(1\) | H-phosphonates \(2\) | Product \(3\) |
|------------------|------------------|--------------|
| \(X = \text{Br}\) | \(X = \text{Cl}\) | \(X = \text{I}\) |
| 3ag | \(X = \text{Br}\), 71% | \(X = \text{Cl}\), 64% |
| 3ah | \(X = \text{I}\), 83% |
| 3ai | \(X = \text{Br}\), 64% |
| 3aj | \(X = \text{Br}\), 71% |
| 3ak | \(X = \text{I}\), 67% |
| 3al | \(X = \text{Br}\), 78% |
| 3am | \(X = \text{Br}\), 91% |

| Aryl halide \(1\) | H-phosphonates \(2\) | Product \(3\) |
|------------------|------------------|--------------|
| \(X = \text{Br}\) | \(X = \text{Cl}\) | \(X = \text{I}\) |
| 3an | \(X = \text{Br}\), 51% |
| 3ao | \(X = \text{Br}\), 85% |
| 3ap | \(X = \text{Br}\), 91% |
| 3aq | \(X = \text{Br}\), 71% | \(X = \text{I}\), 88% |
| 3ar | \(X = \text{Br}\), 69% |
| 3as | \(X = \text{Br}\), 72% | \(X = \text{I}\), 76% |

*Reaction conditions: aryl halide \(1\) (0.2 mmol), H-phosphonates \(2\) (0.3 mmol), NiCl\(_2\)-dme (0.02 mmol), ligand (0.02 mmol), K\(_3\)PO\(_4\) (2 equiv.), \(\text{Bu}_4\text{NBr}\) (4 equiv.) in 4.0 mL DMA at room temperature for 12 h, \(i = 2\) mA, \(j = 1\) mA cm\(^{-2}\), \(t, 12\) h. GFE = graphite felt electrode, FNE = foamed nickel electrode; yields after purification. *Aryl halide \(1\) (0.4 mmol) and H-phosphonates \(2\) (0.2 mmol) were used. The *\(\text{Bu}_3\)N (2 equiv.) was used as base. The DIPEA (2 equiv.) was used as base. The reaction was performed on 0.1 mmol scale.
observed, which corresponded to the Ni\textsuperscript{II}/Ni\textsuperscript{III} redox potential. Next, diphenylphosphine oxide \(2a\) and the base, \(\text{K}_3\text{PO}_4\), were added to the solution. After stirring for 2 min, the peak was shifted to a higher potential, and the current increased significantly (Scheme 2f, Condition D), indicating the formation of new Ni\textsuperscript{II} species after transmetalation (Ar–Ni\textsuperscript{II}–P(O)Ph\textsubscript{2}). Moreover, after an additional 8 min of stirring, no current increase was observed, showing the transmetalation step completed within 2 min. This was supported by the density functional theory (DFT) calculation, in which the transmetalation step acquired an energy barrier of only 1.7 kcal/mol (Scheme 3a, Condition D).

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D to D-TS). The in-situ generated Ni\textsuperscript{ii}(bpy), as well as the electrolyte, Bu\textsubscript{4}NPF\textsubscript{6}, gave no oxidation peak, which confirmed further the two reversible Ni\textsuperscript{ii}/Ni\textsuperscript{iii} peaks in conditions C and D. By monitoring the reaction progress and representing the yield versus reaction time based on 3z (0.2 mmol), we showed that the reaction completed within 90 min, with 95% GC yield, when 2 mA current was applied. In contrast, the reaction only gave 1% GC yield without electricity after 90 min. Noteworthily, the current efficiency was 170%, which suggested that this transformation employed not only an electro-assisted Ni\textsuperscript{ii}/Ni\textsuperscript{iii} catalytic cycle but also a non-electro-assisted Ni/Ni\textsuperscript{ii} catalytic pathway (Scheme 2d).

When the reaction of 1z and 2a was conducted under the standard experimental conditions for 20 min, the product was obtained in 29% yield. Prolonging the reaction without electricity for 12 h resulted in a 38% yield (Scheme 2c). These results indicate that the electricity was necessary for this reaction in order to regenerate the Ni\textsuperscript{ii} and Ni\textsuperscript{iii} complexes, which were converted to Ni\textsuperscript{ii} complexes by the thermodynamically favored comproportionation (see also Scheme 3c). Additionally, we performed detailed DFT-based calculations to support the experimental mechanistic studies further (Scheme 3a; see Section 7.1−“Computational Methods” in Supporting Information). As a model system, we selected the cross-coupling reaction between phenyl bromide and diphenylphosphine oxide catalyzed by Ni(bpy). First, the ligand bpy coordinated to the Ni\textsuperscript{ii} precatalyst, followed by cathodic reduction to form the active Ni\textsuperscript{0} catalyst B. The catalytic process started with the oxidative addition of phenyl bromide to the active Ni\textsuperscript{0} catalyst B via transition state B-TS with an energy barrier of 9.5 kcal/mol. Then the deprotonated diphenylphosphine oxide coordinates to the Ni\textsuperscript{ii} intermediate C. The generated Ni\textsuperscript{ii} intermediate D underwent transmetalation via the transition state D-TS. In the next step, the Ni\textsuperscript{ii} species E was oxidized by the anode, together with the cathodic reduction of the Ni\textsuperscript{ii} intermediate G, a redox process facilitated by electricity. Finally, the reductive elimination of Ni\textsuperscript{ii} afforded the C-P bond cross-coupling product with an energy barrier of only 3.8 kcal/mol. Alternatively, the non-electro-assisted pathway was also investigated by DFT-based calculations (Scheme 3b). First, transmetalation of diphenylphosphine oxide to Ni\textsuperscript{ii} intermediate G via transition state H-TS affored Ni\textsuperscript{ii} complex I. Subsequently, the Ni\textsuperscript{ii} intermediate F was formed via oxidative addition with an energy barrier of 19.0 kcal/mol, followed by reductive elimination to afford the cross-coupling product. It should be pointed out that the unstable Ni\textsuperscript{ii} and Ni\textsuperscript{iii} intermediates (F and G) were converted easily to Ni\textsuperscript{ii} complexes by comproportionation reaction, since this process was exothermic and thermodynamically favored (Scheme 3c, ΔG = −8.4 kcal/mol), further demonstrating the requirement of electricity. The calculation of the oxidative addition of the phenyl bromide to the Ni\textsuperscript{ii}-halide species was also carried out (Scheme 3d). We found that the energy barrier for the reaction was considerably higher than that of the Ni\textsuperscript{0} complex (B-TS vs G-TS, 25.8 kcal/mol vs 9.5 kcal/mol).

Given that the less-reactive aryl chloride was also a suitable substrate, we calculated the oxidative addition of 4-chlorobenzenonitrile to the Ni\textsuperscript{ii} and Ni\textsuperscript{iii} complexes. The results showed that the oxidative addition of aryl chloride to the Ni\textsuperscript{ii} achieved an energy barrier of 15.1 kcal/mol (B-TS2). However, the energy barrier of the oxidative addition to the Ni\textsuperscript{ii} was 31.7 kcal/mol (G-TS2), which was not feasible at room temperature. Additionally, the generated intermediate after oxidative addition at Ni\textsuperscript{ii} was much more stable than that with Ni\textsuperscript{ii} (C vs K, −34.5 kcal/mol vs 21.4 kcal/mol; C2 vs K2, −33.1 kcal/mol vs 22.3 kcal/mol), which also indicated that the oxidative addition to Ni\textsuperscript{0} was thermodynamically favored. Further, the oxidative addition energy barrier to Ni\textsuperscript{ii} dimer was calculated to be 25.4 kcal/mol (L-TS), similar to the barrier attained by the Ni\textsuperscript{ii} monomer (Scheme 3e). The conventional reductive elimination energy barrier for the C-P bond formation of Ar-Ni\textsuperscript{ii}-P(O)Ph\textsubscript{2} was calculated to be 20.3 kcal/mol, which was considerably higher, compared with that of the Ni\textsuperscript{ii} intermediate (3.8 kcal/mol). Collectively, these results showed that the reductive elimination for the C-P bond formation with Ni\textsuperscript{ii} was kinetically preferred, indicating an essential role of electricity in the Ni-catalyzed C-P bond formation (Scheme 4). In order to investigate the universality of this phenomenon in electro-assisted nickel-catalyzed C-heteroatom bond formation reactions, we carried out further calculations of the reductive elimination energy barriers for a series of Ni\textsuperscript{ii} and Ni\textsuperscript{iii} reaction intermediates with varying nucleophile types. Amine (19.8 kcal/mol at Ni\textsuperscript{ii}, 0.7 kcal/mol at Ni\textsuperscript{iii}), alcohol (29.5 kcal/mol at Ni\textsuperscript{ii}, 10.0 kcal/mol at Ni\textsuperscript{iii}), lactam (31.1 kcal/mol at Ni\textsuperscript{ii}, 4.8 kcal/mol at Ni\textsuperscript{iii}), ammonia (17.9 kcal/mol at Ni\textsuperscript{ii}, 2.2 kcal/mol at Ni\textsuperscript{iii}), water (33.2 kcal/mol at Ni\textsuperscript{ii}, 10.5 kcal/mol at Ni\textsuperscript{iii}), thiophenol (33.1 kcal/mol at Ni\textsuperscript{ii}, 2.2 kcal/mol at Ni\textsuperscript{iii}), benzene-selenol (32.6 kcal/mol at Ni\textsuperscript{ii}, 0.2 kcal/mol at Ni\textsuperscript{iii}); we observed that they were all in line with this result trend. Besides this observation, we analyzed the stability of the products and Ni-intermediates, which formed after the reductive elimination at Ni\textsuperscript{ii} and Ni\textsuperscript{iii} states (see Sections 7.2 and 7.3 in Supporting Information). Our calculations showed that the reductive elimination process at Ni\textsuperscript{ii} was endothermic whereas that at Ni\textsuperscript{iii} was exothermic (for phosphonate, 0.6 kcal/mol at Ni\textsuperscript{ii} and −42.3 kcal/mol at Ni\textsuperscript{iii}; for amine, 1.8 kcal/mol at Ni\textsuperscript{ii} and −59.2 kcal/mol at Ni\textsuperscript{iii}; for alcohol, 10.7 kcal/mol at Ni\textsuperscript{ii} and −50.1 kcal/mol at Ni\textsuperscript{iii}; for lactam, 12.6 kcal/mol at Ni\textsuperscript{ii} and −47.5 kcal/mol at Ni\textsuperscript{iii}; for ammonia, −0.2 kcal/mol at Ni\textsuperscript{ii} and −57.9 kcal/mol at Ni\textsuperscript{iii}; for water, 15.4 kcal/mol at Ni\textsuperscript{ii} and −48.1 kcal/mol at Ni\textsuperscript{iii}; for thiophenol, 20.7 kcal/mol at Ni\textsuperscript{ii} and −34.3 kcal/mol at Ni\textsuperscript{iii}; for benzene-selenol, 20.3 kcal/mol at Ni\textsuperscript{ii} and −28.6 kcal/mol at Ni\textsuperscript{iii}). Thus, we demonstrate that Ni\textsuperscript{iii}
Scheme 3 | DFT-computed energy profiles for the electro and nickel dual-catalyzed C–P bond formation reaction of aryl halides and H-phosphonates. Free energies in solution (in kcal·mol\(^{-1}\)) at the SMD(DMA)-MN15/Def2-QZVPP/\(\omega\)B97x-D/Def2-TZVP(Ni)/Def2-SVP (other atoms) level are displayed. Selected DFT geometries are listed. Bond lengths are in Å. (a). Energy profile of the main catalytic pathway. (b). Energy profile of the nonelectro-assisted NiI/NiIII catalytic pathway. (c). Comproportionation reaction of Ni\(^{\text{II}}\) complex. (d). Oxidative addition energy barrier of aryl chloride and aryl bromide to Ni\(^{\text{0}}\) or Ni\(^{\text{I}}\) complex. (e). Oxidative addition energy barrier of aryl bromide to Ni\(^{\text{II}}\) dimer.
complexes are more prone to undergo reductive elimination from both kinetic and thermodynamic point of view, further emphasizing the importance of electrolysis in the development of nickel-catalyzed cross-coupling reactions under mild conditions.

**Conclusion**

Redox-neutral cross-coupling reactions have been realized for the C–P and C–Se bond formations via merging paired electrolysis and nickel catalysis. With the assistance of electricity, the catalysis proceeded efficiently under mild conditions, and thus, possessed a broad substrate scope. Aryl halides bearing ortho-substituents, active free amines, heterocycles, and complex motifs could all be converted to the corresponding phosphorylated derivatives. Moreover, the substrate scope was not limited to aryl iodides and aryl bromides only, inactivated aryl chlorides and vinyl halides could also be applied. Notably, a series of experimental mechanistic investigations and DFT calculations support a Ni⁰/NiII/NiIII/NiI catalytic cycle. The simultaneous anodic oxidation of NiII to NiIII and cathodic reduction of NiI to Ni⁰ occurred with high energy efficiency. In addition, DFT calculations for different C–heteroatom bond formations showed a general trend in which the electricity promoted the reduction of the energy barrier of the Ni-catalyzed electrochemical transformations.

**Supporting Information**

Supporting Information is available.
**Conflict of Interest**

The authors declare no competing financial interests.

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