**Cross-Coupling**

# Nickel-Catalyzed Cross-Coupling of Styrenyl Epoxides with Boronic Acids**

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Epoxides are invaluable substrates for complex molecule synthesis owing to their ready accessibility from alkene- and carbonyl-containing chemical feedstocks and their proclivity toward ring opening by a variety of nucleophiles.[1] Despite recent advances, reactions with carbon-centered nucleophiles are typically limited to the use of stabilized carbanions, strong organometallic reagents, or π-rich arenes.[2] The identification of a catalyst system capable of engaging epoxides and boronic acids in C−C bond formation would be an attractive alternative because of the low toxicity, high functional group tolerance, and commercial availability of boron-based nucleophiles. While palladium-catalyzed allylic substitutions of vinyl epoxides and boronic acids have been documented,[3,4] reactions with simple aromatic or aliphatic epoxides have not been reported. Nonetheless, insertion of transition metals into the $C_{sp^3}$−O bonds of unactivated epoxides has been realized in stoichiometric studies[5] and proposed in a few catalytic transformations, including epoxide carbonylation,[6] carboxylation,[7] halogenation,[8] isomerization,[9] and reductive coupling.[10] Herein, we describe our initial studies directed at the development of cross-coupling reactions between epoxides and boronic acids by nickel(0)-catalyzed C−O activation. We report that 10 mol% of a biarylmonophosphine-ligated nickel complex affords good efficiency for reactions between styrenyl epoxides and a variety of aryl boronic acids. Unlike ring opening with most organometallic reagents, this transformation provides access to α-substituted rather than β-substituted alcohol products. Mechanistic studies support a multicatalytic sequence involving epoxide isomerization to an η²-oxanickellacycle by benzylic $C_{sp^3}$−O bond oxidative addition, followed by nickel-catalyzed 1,2-arylation.

Styrenyl epoxide compounds were chosen as substrates for initial studies because of their commercial availability and potential bias toward oxidative addition at the activated benzylic position.[11] On the basis of recent studies on C−O bond activation,[12] we first examined [NiCl₂(PCy₃)₂] as a

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catalyst precursor for the coupling of *p*-tol styrene oxide and PhB(OH)₂; gratifyingly, the cross-coupled product was observed, albeit in low yield (Table 1, entry 1). To assess the role of various phosphine ligands, [Ni(cod)₂] was next evaluated as a metal source. With PCy₃, reaction efficiencies remained poor (Table 1, entry 2). However, catalyst complexes arising from [Ni(cod)₂] and dialkylbiaryl monophosphine ligands led to improved reaction efficiency (Table 1, entries 3–5), consistent with the ability of sterically hindered, electron-rich ligands to facilitate difficult oxidative insertions.[13] Among the ligands tested, BrettPhos proved most effective, and afforded the coupled product in 88% yield (Table 1, entry 5).[14] To our knowledge, this reaction represents the first application of this ligand to a nickel-catalyzed process.

A survey of other reaction parameters indicated that the use of K₃PO₄ as base and toluene/water (1:0.16) as solvent was optimal. Particularly noteworthy was the dependence of the reaction outcome on the identity of the boronate nucleophile; phenyl boronic acid was considerably more effective than phenyl boroxine, whereas phenyl trifluoroborate was inactive (compare Table 1, entries 5–7). To account for these data, we propose that coordination or protonation by the boronic acid

***Table 1:*** Optimization studies for the coupling of *p*-tol styrene oxide and phenyl boronic acid.[a]
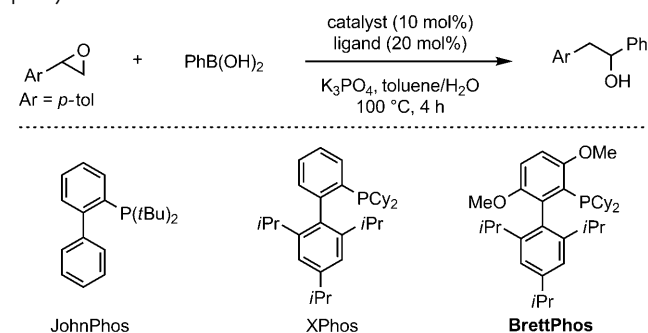


| Entry | Catalyst | Ligand | Nucleophile | Yield [%][b] |
|---|---|---|---|---|
| 1 | [NiCl₂(PCy₃)₂] | None | PhB(OH)₂ | 13 |
| 2 | [Ni(cod)₂] | PCy₃ | PhB(OH)₂ | 21 |
| 3 | [Ni(cod)₂] | JohnPhos | PhB(OH)₂ | 67 |
| 4 | [Ni(cod)₂] | XPhos | PhB(OH)₂ | 68 |
| **5** | **[Ni(cod)₂]** | **BrettPhos** | **PhB(OH)₂** | **88** |
| 6 | [Ni(cod)₂] | BrettPhos | (PhBO)₃ | 20 |
| 7 | [Ni(cod)₂] | BrettPhos | PhBF₃K | 0 |

[a] Reaction conditions: epoxide (1.0 equiv), PhB(OH)₂ (4.0 equiv), base (4.5 equiv), H₂O (30 equiv). For further evaluation of reaction parameters, see the Supporting Information. [b] Yields determined by HPLC using methyl benzoate as a quantitative internal standard; average of two runs. Cy = cyclohexyl, cod = cycloocta-1,5-diene, *p*-tol = *p*-tolyl.

facilitates oxidative addition of the epoxide to the nickel catalyst.[15] Boron to nickel transmetalation may also be accelerated through formation of a reactive "ate" complex. This proposal is in agreement with recent studies on the stoichiometric reaction of aryl boronic acids with a rhoda-oxetane complex.[16]

Observation of α-substituted alcohols as the major products in these reactions can be explained by initial oxidative addition to access metallaoxetane **1**[17,18] or its ring-opened form, followed by β-hydride elimination and reinsertion to afford $\eta^2$-oxanickellacycle **2** (Scheme 1).[19] Kulasegaram and Kulawiec[20a,b] have disclosed studies on palladium-catalyzed epoxide isomerization that lend support to this proposal.[20c–e, 21] Subsequent nickel-catalyzed 1,2-arylation with boronic acids, a transformation demonstrated recently by the research groups of Itami and Aoyama,[22a,b] would deliver the observed product.[22c–g] While the rearrangement and arylation reactions are known separately, a simple catalyst capable of effecting both elementary steps has not been identified. Indeed, development of a catalyst system that performs both operations in a single pot from easily accessed and relatively stable epoxides avoids the synthesis and handling of aryl acetaldehydes, which are inconvenient substrates owing to their significant instability on the bench.

Although formation of the aldehyde intermediate could proceed by thermal or Lewis acid catalyzed rearrangement of the epoxide, the following data favor a redox pathway involving oxidative addition. First, preliminary initial rate studies indicate that the reaction displays a first order dependence on [Ni(cod)$_2$]. In addition, we find that phenyl-acetaldehyde undergoes efficient 1,2-arylation at lower temperatures than styrene oxide and we detect no buildup of aldehyde during the reaction course. Taken together, these data suggest that initial isomerization to phenylacetaldehyde is nickel catalyzed and rate determining. While this does not preclude rate-limiting Lewis acid catalyzed rearrangement, Ni$^{II}$ complexes are generally more effective Lewis acids than Ni$^0$ complexes, especially those ligated with electron-releasing ligands such as BrettPhos.[23] Notably, use of catalysts that are more Lewis acidic than Ni$^0$/BrettPhos, such as Ni$^0$/PPh$_3$ or Ni$^{II}$ salts, afforded decreased yields (see the Supporting Information for details).[24]
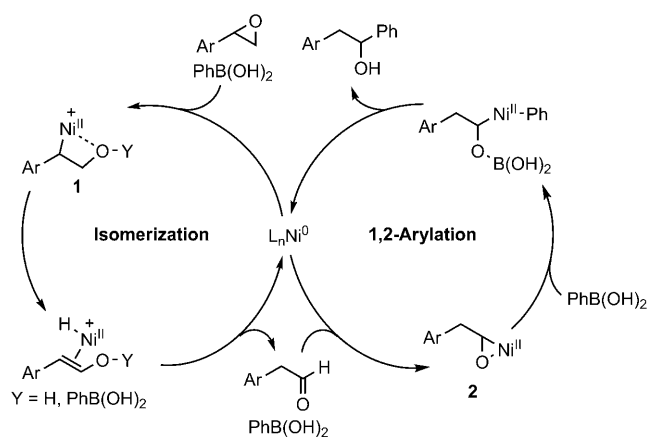
**Scheme 1.** Proposed catalytic cycle.

Additional support for the redox role of nickel in epoxide activation was derived from red crystals of a catalytically active Ni$^{II}$ complex obtained from a catalytic reaction. The structure of this air-stable complex was elucidated by X-ray crystallographic analysis, and shows a remarkable 1:1:1:1 combination of Ni$^{II}$, BrettPhos, styrene oxide, and phenyl boroxine, wherein the biaryl phosphine ligand has formally undergone cyclometalation with the epoxide and Ni$^0$ (Figure 1).[25,26] Observation of an induction period when
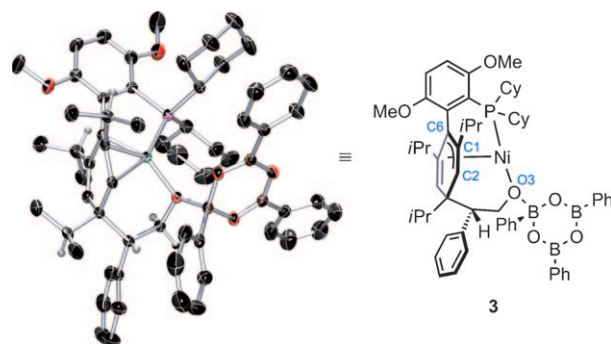
**Figure 1.** ORTEP plot of complex **3**. Thermal ellipsoids are drawn at 30% probability and selected hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: Ni–P 2.1986(5), Ni–C6 1.9698(15), Ni–C1 1.9789(15), Ni–C2 2.0459(15), Ni–O3 1.9172(11), P-Ni-C6 87.72(5), C6-Ni-C2 72.67(6), C2-Ni-O3 91.50(5), O3-Ni-P 110.40(4).

10 mol% of **3** was used as a catalyst suggests that **3** is not directly in the catalytic cycle (Figure 2, see the Supporting Information for details).[27] However, use of **3** as the catalyst for the reaction of *p*-fluoro styrene oxide with phenyl boronic acid afforded good yields of products derived from both styrene oxide and *p*-fluoro styrene oxide, thus indicating that the epoxide incorporated into the metallacycle undergoes productive reaction (for clarity, the yield of **5** in Figure 2 is normalized out of a theoretical maximum of 0.0075 mmol). Clearly, these data suggest that **3** accesses the catalytic cycle and supports nickel oxidative addition into a C$_{sp^3}$–O bond as a viable catalytic step.[28]

Based on these data, we suggest that **3** arises from ring expansion of nickellaoxetane **1**. Alternatively, oxidative cyclization of the ligand, epoxide, and Ni$^0$ could directly access **3**, which would then undergo a 1,2-hydride shift to generate $\eta^2$-oxanickellacycle **2**.[29] Additional studies are in progress to further clarify the mechanism of this process and to determine if conditions can be identified that disfavor β-hydride elimination, and therefore resulting in a direct cross-coupling reaction between epoxides and organometallic reagents.

With insight gained from mechanistic analysis, we investigated the scope of the reaction (Table 2). Generally, styrenyl epoxides containing *p*- and *m*-substituents performed well under the standard reaction conditions. More hindered epoxides, including *o*-tolyl styrene oxide and *o*-fluoro styrene oxide, also underwent coupling with phenyl boronic acid, albeit with slightly depressed yields. Substrates bearing strongly electron-releasing groups, however, fared poorly, likely as a result of the instability of the oxirane to prolonged heating at 100°C. To date, reactions with non-styrenyl
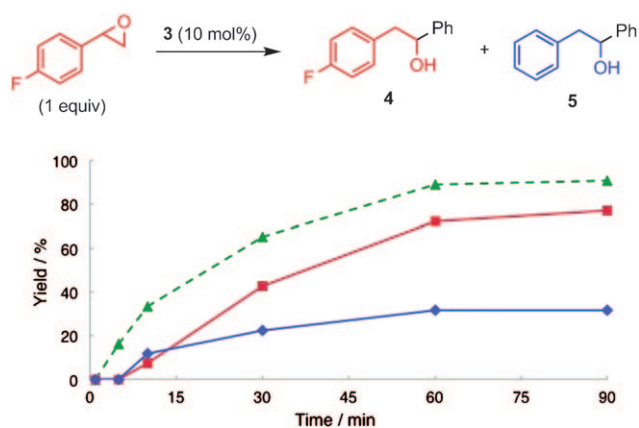
**Figure 2.** Yield of **4** (■) and **5** (◆) (calculated from a theoretical maximum of 0.0075 mmol) for a reaction catalyzed by **3** compared to a [Ni(cod)$_2$]/BrettPhos-catalyzed reaction (▲). Standard reaction conditions: [Ni(cod)$_2$] (10 mol%), BrettPhos (20 mol%), epoxide (1.0 equiv), PhB(OH)$_2$ (4.3 equiv), base (4.8 equiv), H$_2$O (30 equiv), on a 0.3 mmol reaction scale. Conditions using **3** as a catalyst: **3** (10 mol%), BrettPhos (10 mol%), epoxide (1.0 equiv), PhB(OH)$_2$ (4.0 equiv), base (4.8 equiv), H$_2$O (30 equiv), on a 0.075 mmol reaction scale. Yields determined by HPLC using methyl benzoate as a quantitative internal standard.

terminal epoxides have proven unsuccessful, which is in agreement with the high activation barrier for oxidative addition to aliphatic C$_{sp^3}$–O bonds.

Evaluation of boronic acid coupling partners has revealed that a variety of nucleophiles are amenable to the reaction (Table 3). Both electron-rich and electron-poor aryl boronic acids are well tolerated. Particularly notable in this regard is the use of *p*-methoxy phenyl boronic acid, as aryl methyl ethers have been reported to undergo Suzuki–Miyaura coupling reactions catalyzed by related nickel complexes.[30] Unfortunately, heteroaromatic and carbonyl-containing aryl boronic acids afford minimal product.[31] Despite this limi-

**Table 2:** Coupling of substituted styrene oxides with PhB(OH)$_2$.[a]



| Entry | Product | Yield [%][b] | Entry | Product | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | | 77 | 6 | | 73 |
| 2 | | 50 | 7 | | 46 |
| 3 | | 66 | 8 | | 60 |
| 4 | | 74 | 9 | | 66 |
| 5 | | 67 | 10 | | 0 |

[a] Reaction conditions: epoxide (1.0 equiv), PhB(OH)$_2$ (4.0 equiv), K$_3$PO$_4$ (4.5 equiv), H$_2$O (30 equiv). [b] Yield of isolated product on a 0.3 mmol reaction scale; average of two runs.

**Table 3:** Coupling of *p*-tol styrene oxide with various boronic acids.[a]



| Entry | Product | Yield [%][b] | Entry | Product | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | | 59 | 6 | | 57 |
| 2 | | 55 | 7 | | 77 |
| 3 | | 68 | 8 | | 59 |
| 4 | | 49 | 9 | | 58 |
| 5 | | 50 | 10 | | 60 |

[a] Reaction conditions: epoxide (1.0 equiv), PhB(OH)$_2$ (4.0 equiv), K$_3$PO$_4$ (4.5 equiv), H$_2$O (30 equiv). [b] Yield of isolated product on a 0.3 mmol reaction scale; average of two runs.

tation, the transformation provides a method for performing a tandem isomerization/arylation reaction in one pot, thus allowing access to synthetically valuable secondary alcohols from readily available and inexpensive terminal epoxides.

In summary, we have developed a new benzylic C$_{sp^3}$–O activation protocol that enables the catalytic functionalization of epoxides with unstabilized carbon-centered nucleophiles. Evidence suggests that the reaction proceeds through a nickellaoxetane, which has promise as a valuable synthetic intermediate in a variety of C–C bond-forming manifolds. To this end, studies with alternative nucleophiles are underway, and work toward expanding the substrate scope to include a wider variety of epoxide substrates will be reported in due course.

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[27] The catalytic viability of Ni⁰/PCy₃ also supports this conclusion.

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