JOC The Journal of Organic Chemistry

Article

Nickel-Catalyzed Hydroarylation of Alkynes Under Reductive Conditions with Aryl Bromides and Water

E. Ryan Barber, Hannah M. Hynds, Claudia P. Stephens, Holli E. Lemons, Emily T. Fredrickson, and Dale Wilger

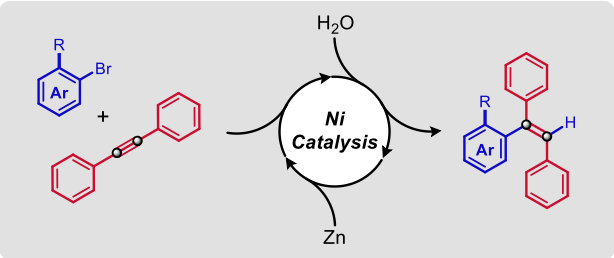
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b01556 • Publication Date (Web): 21 Aug 2019

Nickel-Catalyzed Hydroarylation of Alkynes Under Reductive Conditions with Aryl Bromides and Water

E. Ryan Barber,‡ Hannah M. Hynds,‡ Claudia P. Stephens,‡ Holli E. Lemons, Emily T. Fredrickson, Dale J. Wilger*

Department of Chemistry and Biochemistry, Samford University, Birmingham, Alabama 35229, United States

*E-mail: dwilger@samford.edu



ABSTRACT: An operationally simple nickel-catalyzed hydroarylation reaction for alkynes is described. This three-component coupling reaction utilizes commercially available alkynes and aryl bromides, along with water and Zn. An air-stable and easily synthesized Ni(II) precatalyst is the only entity used in the reaction that is not commercially available. This reductive cross-coupling reaction displays a fairly unusual *anti* selectivity when aryl bromides with *ortho* substituents are used. In addition to optimization data and a preliminary substrate scope, complementary experiments including deuterium labeling studies are used to provide a tentative catalytic mechanism. We believe this report should inspire and inform other Ni-catalyzed carbofunctionalization reactions.

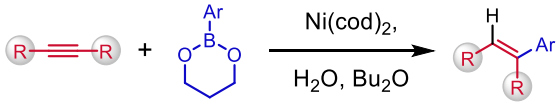
Introduction

Alkenes are ubiquitous building blocks in nearly all areas of synthetic chemistry. Alkene syntheses are allocated significant attention in both graduate and undergraduate chemistry courses because of their importance. Ni- and Pd-catalyzed reactions play key roles in both the industrial synthesis of low-molecular-weight alkenes, and in the specialty synthesis of more elaborate and highly-substituted alkenes.[1,2] More specifically, the synthesis of alkenes with aromatic substituents is of high importance in materials applications and in pharmaceutical chemistry (e.g., tamoxifen). Transition-metal-catalyzed reactions which feature the carbometalation of alkynes have become a focal point for alkene synthesis because these processes often allow for regioselectivity and stereoselectivity to be controlled in the products. This is a critical requirement for the synthesis of nearly any functional alkene. Various transition metals including Cr,[3] Mn,[4] Fe,[5] Co,[6] Ni,[7] Cu,[8] Rh,[9] and Pd[10] have all been used as catalysts for alkene synthesis in this fashion. Frequently, an organometallic reagent containing Li, B, Mg, Zn, or Sn is added to the alkyne, although other reagents including carbon dioxide[11] and organohalides[12] can undergo addition as well if a stoichiometric reductant is included. Additionally, modern chemical technology allows alkyne hydroarylation through the direct activation of C–H bonds.[13]

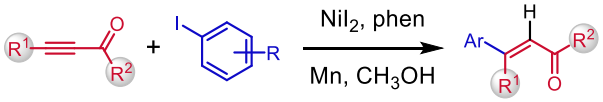
Alkene syntheses which rely on transition-metal-catalyzed carbometalation inevitably require an electrophilic reagent in order to capture the transiently formed organometallic intermediate. If a protic compound such as water is used as the terminal electrophile, then a hydrogen substituent results in the product.[3,4,5,6,7d,e,8a,9,10] In certain instances the reagent responsible for carbometalation can be combined in the same flask with the

Scheme 1. Ni-Catalyzed Hydroarylation Reactions

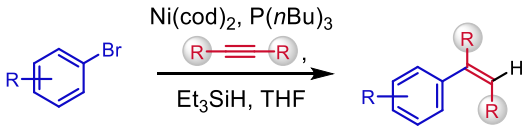
a) Shirakawa, Takahashi, Tsuchimoto, Kawakami:[16]



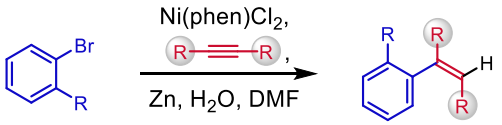
b) Dorn, Olsen, Kelemen, Shrestha, Weix:[12]



c) Robbins & Hartwig:[17]



d) ***This work*** (hydroarylation with ArBr, Zn, and H_2O):



electrophile so as to affect an efficient three-component coupling reaction. Three-component coupling reactions involving alkynes and organometallic reagents are more common with the second-row transition metals Rh[9a-c] and Pd[10] because less reactive organometallic reagents (such as boronic acids) will participate in transmetalation with these metals; the reagents responsible for transmetalation and electrophilic trapping are more likely to be compatible in the same reaction flask. Still, there are several interesting reports of three-component reactions that involve carbometalation across an alkyne catalyzed by first-row transition metals such as Co and Ni.[7f,11,12,14]

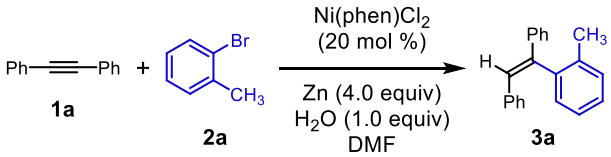
A fairly ubiquitous feature of transition-metal-catalyzed carbometalation reactions is that addition to the alkyne occurs with *syn* selectivity. When considering hydroarylation, an important class of reactions for synthesizing alkenes, most procedures produce alkenes that demonstrate this *syn* selectivity. There have been very few exceptions. Several reports by Fujiwara and Nolan have detailed Pd-catalyzed hydroarylation reactions that give *trans*-stilbene products when trifluoroacetic acid is used as a solvent.[15] These Pd-catalyzed reactions are proposed to occur via an electrophilic metalation mechanism and they require arenes possessing an inherently high nucleophilicity. The reaction conditions (with trifluoroacetic acid used as a solvent) would also be expected to limit the substrate scope of these reactions. Most Ni-catalyzed hydroarylation reactions have demonstrated *syn* selectivity. Kawakami and coworkers have demonstrated a *syn*-selective hydroarylation reaction using aryl boronic acids with $Ni(cod)_2$ as a precatalyst (Scheme 1a).[16] Weix and coworkers have reported a *syn*-selective hydroarylation reaction of alkynoates with aryl iodides under reductive conditions (Scheme 1b).[12] Both Kawakami and Weix propose catalytic turnover by protonolysis of a vinyl nickel intermediate. To the best of our knowledge, *syn* selectivity is observed in all disclosed Ni-catalyzed alkyne hydroarylation reactions except for a single report from the Hartwig group.[17] Hartwig and Robbins report two different sets of conditions for *anti*-selective alkyne hydroarylation. One preparation employs aryl boronic acids with triphenylphosphine as a ligand (not shown), and the second requires aryl bromides with tributylphosphine serving as the ligand and triethylsilane serving as the terminal reductant (Scheme 1c). Both sets of conditions reported by the Hartwig group use the Ni(0) precatalyst $Ni(cod)_2$, which is moisture, light, and air-sensitive. Ni-catalyzed C–C bond-forming reactions have seen explosive growth in recent years,[18] and reductive cross-coupling reactions in particular have benefited from significant development.[19] Given the success of these approaches, we hypothesized that reductive coupling conditions with a Ni catalyst might be able to provide an *anti*-selective hydroarylation reaction with air-stable and commercially available precursors (Scheme 1d).

Results and Discussion

Our initial investigation began by examining the hydroarylation of diphenylacetylene (**1a**) with various aryl halides, reductants, protic reagents, solvents, and Ni(II) precatalysts containing bipyridyl ligands. After extensive screening, we determined that hydroarylation was effective if a precatalyst containing the 1,10-phenanthroline ligand ($Ni(phen)Cl_2$) was employed in conjunction with water as the electrophilic trapping reagent. *N*,*N*-Dimethylformamide (DMF) was the optimal solvent. The precatalyst $Ni(phen)Cl_2$ is air-stable and easily prepared in one step from inexpensive commercially available precursors. We selected the hydroarylation of **1a** with *ortho*-bromotoluene (**2a**) for optimization (Table 1) because the use of **2a** allowed the diastereoselectivity of the reaction to be measured. We were further encouraged by the fact that Ni(II) aryl halide complexes with *ortho*-substituted aryl ligands are well known.[20] We felt that the ability to synthesize and manipulate potential catalytic intermediates as air-stable species might facilitate insightful mechanistic studies.

We found that the hydroarylation of **1a** was effective when 3.0 equiv of the aryl bromide **2a** were used along with 4.0 equiv of Zn and 1.0 equiv of H_2O (entry 1). Reactions were typically prepared in an inert-atmosphere glove box, but yields were acceptable if no effort was made to exclude air or moisture (entries 2 and 3). Lower yields for **3a** were observed if only 1.0 equiv

Table 1. Optimization Data for the Ni-Catalyzed Hydroarylation of Diphenylacetylene (1a)



entry	conditions[a]	% yield **3a** (*Z*/*E* ratio)[b]
1	**optimized**	***73*[c] (8.2:1)**
2	N_2 sparge	58%[c] (7.4:1)
3	air	52%[c] (6.5:1)
4	1 equiv **2a**	55%[c] (6.9:1)
5	10% Ni	72%[c] (7.2:1)
6	5% Ni	49%[c] (7.4:1)
7	no H_2O	48%[c] (6.9:1)
8	bromobenzene (**2b**)	65%[d] (**3b**)
9	*ortho*-chlorotoluene	<5%[c]
10	2-bromomesitylene	<5%[c]
11	4-octyne	<5%[c]
12	$Ni(phen)Br_2$	74%[d,e] (8.1:1)
13	$Ni(bpy)Cl_2$	58%[c] (8.2:1)
14	$Ni(^tBubpy)Cl_2$	46%[d] (12:1)
15	CH_3OH solvent at 50 °C	26%[c] (5.7:1)

[a] Reactions were prepared under N_2 using 1.0 equiv of **1a**, 3.0 equiv **2a**, 4.0 equiv Zn, 1.0 equiv H_2O, 20 mol % $Ni(phen)Cl_2$, and DMF (0.1 M). Reactions were heated at 70 °C (14-24 hours). [b] The *Z*/*E* ratio was determined by ^1H NMR. [c] Yield calculated by GC-MS. [d] Refers to isolated yields on the 1.12 mmol scale. [e] Reaction time was 48

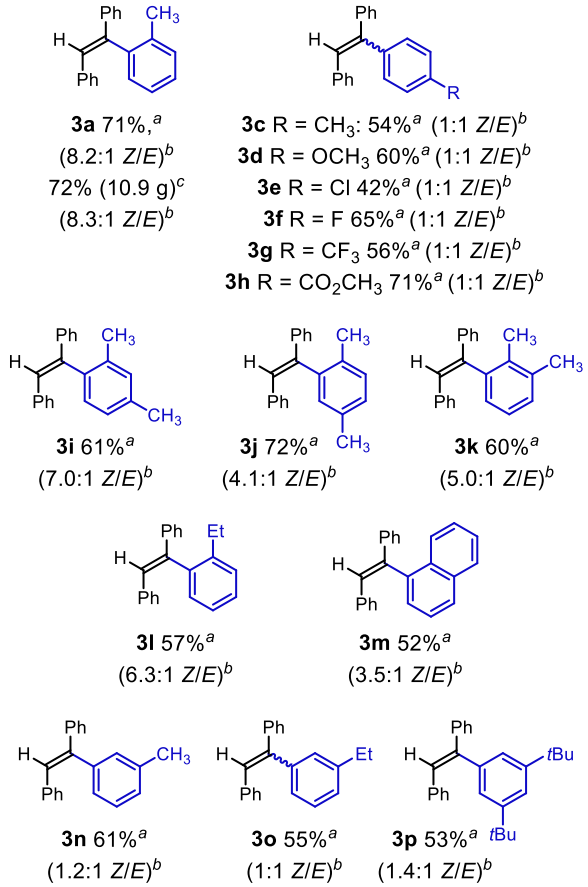
of the aryl bromide was used (entry 4). The optimized hydroarylation reaction was not overly sensitive to the precatalyst loading (entries 5 and 6), although a 20% precatalyst loading was superior for several aryl halides used later in this study.[21] While H_2O is required for high-yielding hydroarylation reactions, there is a significant background reaction even when rigorously dried solvents are used (entry 7). The omission of H_2O from the optimized reaction conditions also results in a greater number of byproducts, indicating a likely change in mechanism (*vide infra*). The optimized reaction conditions are similarly effective when aryl bromides lacking *ortho* substituents are used (entry 8). The role of H_2O and a preliminary substrate scope for aryl bromides used in the reaction are both described below. The desired product was observed in trace quantities when *ortho*-chlorotoluene was tested as the coupling partner (entry 9). The more sterically hindered di-*ortho*-substituted 2-bromomesitylene was also ineffective (entry 10), as were aliphatic alkynes such as 4-octyne (entry 11). During optimization, commonly observed byproducts included hydrodehalogenation, homocoupling of the aryl bromides, and the semireduction of **1a**.

The identity of the halide counteranion in the precatalyst appears nonconsequential in terms of chemical yield and diastereoselectivity (entry 12).[22] A precatalyst with an unsubstituted bipyridyl ligand (bpy) provides the product in a lower yield with a similar diastereoselectivity (entry 13). Precatalysts containing the 4,4'-di-*tert*-butyl-2,2'-bipyridyl ligand (^{t}Bubpy) provided higher diastereoselectivities, but at the expense of chemical yield (entry 14). Other commercially available ligands did not provide superior chemical yields compared to phenanthroline or superior diastereoselectivity compared to ^{t}Bubpy. The report of *syn*-selective Ni-catalyzed hydroarylation reported by Weix and coworkers used methanol as the solvent and the terminal proton source. The use of anhydrous methanol as a solvent at 50 °C provided a low yield for the desired product (entry 15), but still favored *anti* addition, similar to the other examples in this study. This suggests that the diastereoselectivity is at least partially controlled by the substrate class (tolane derivatives) being examined and not the specific reaction conditions.

The scope of the aryl bromide coupling partner was investigated for the Ni-catalyzed hydroarylation reaction (Table 2). The alkene **3a** could be isolated with good yield and moderate diastereoselectivity up to the decagram scale. Aryl bromides which lack an *ortho* substituent generally provided the alkene product with similar yields, but with little or no diastereoselectivity (**3c**-**h**). The reaction tolerates aryl bromides with electron donating groups (**3c**, **d**). An aryl bromide with a *para*-chloro substituent resulted in a lower yield (**3e**). Competitive hydrodechlorination was responsible for the lower yield in this case and a significant amount of **3b** was observed. Not surprisingly, a *para*-fluoro substituent (**3f**) was well tolerated, presumably due to the greater C–F bond strength. The hydroarylation conditions also tolerated electron withdrawing groups including a trifluoromethyl substituent (**3g**) and a methyl ester (**3h**). The results shown here contrast the protocol described by Hartwig for aryl boronic acids that reported *anti* selectivity for aryl donors that contained only *para* substituents.[17]

Aryl bromides with an *ortho* methyl group provided alkene products in good yields and moderate diastereoselectivities (**3i**, **j**, **k**). The more sterically hindered 1-bromo-2-ethylbenzene provided the corresponding alkene product (**3l**) in a similar

Table 2. Scope of the Aryl Bromide Coupling Partner in the Ni-Catalyzed Hydroarylation of 1a

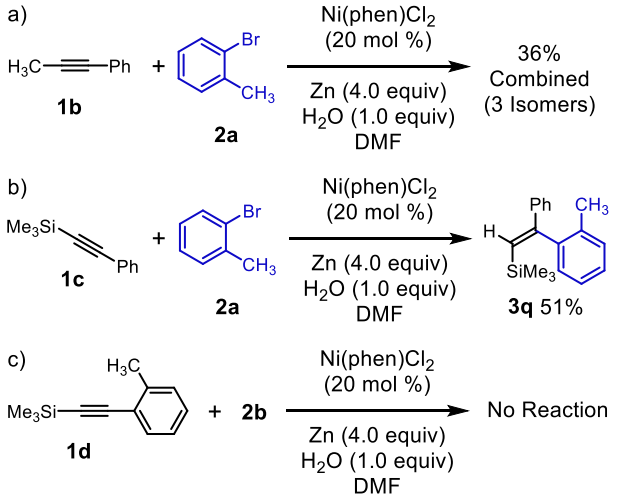


[a] Refers to isolated yields on the 1.12 mmol scale. [b] The *Z*/*E* ratio was determined by ^{1}H NMR. [c] Refers to an isolated yield on the 56 mmol scale (using 10 g of **1a**).

yield and diastereoselectivity, as did the polycyclic substrate 1-bromonaphthalene (**3m**). Somewhat surprisingly, *meta*-bromotoluene provided an alkene product (**3n**) with a lower, yet measurable diastereoselectivity. We did not initially anticipate that a more remote *meta* substituent would influence the diastereoselectivity of this hydroarylation reaction. Even more interesting was that 1-bromo-3-ethylbenzene provided an alkene product (**3o**) with no measurable diastereoselectivity, but 1-bromo-3,5-di-*tert*-butylbenzene provided an alkene product (**3p**) with a diastereoselectivity higher than *meta*-bromotoluene. Most of the aryl bromides studied provided similar chemical yields when a 10 mol % precatalyst loading was examined. For example, the alkenes **3b** and **3c** were produced with lower yields at the reduced precatalyst loading, but the alkenes **3j**, **3l**, and **3n** were produced with similar (± 5%) yields.[23] The diastereoselectivity for this reaction did not depend on the precatalyst loading.

The unusual diastereoselectivity of this hydroarylation reaction prompted us to examine unsymmetrical alkynes as coupling partners. An aromatic substituent was found to be necessary on the alkyne substrate undergoing hydroarylation. The alkyne 1-phenyl-1-propyne (**1b**) produced a mixture of three different alkene isomers in a combined 36% yield (Scheme 2a). Somewhat promisingly, the silyl-protected alkyne 1-phenyl-2-

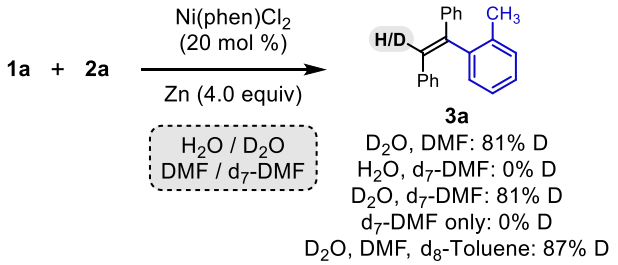
Scheme 2. Unsymmetrical Alkynes in the Ni-Catalyzed Hydroarylation Reaction



trimethylsilylacetylene (**1c**) produced a single alkene regio- and stereoisomer **3q** in a 51% yield (Scheme 2b). The regioselectivity in **3q** can be explained based on the stabilizing effect the trimethylsilyl group is expected to have on the Ni–C bond.[24] Similar regioselectivity has been observed in Pd-catalyzed hydroarylation reactions, although *syn* selectivity was still observed in those reports.[25] The high regioselectivity observed with **1c** provided an opportunity to test whether a similar tolyl-substituted alkyne (**1d**) and bromobenzene (**2b**) would produce the same product by a diastereoconvergent mechanism. Unfortunately, no product was observed under these reaction conditions (Scheme 2c). Our current hypothesis is that the alkyne **1d** fails to undergo migratory insertion due to steric hindrance.

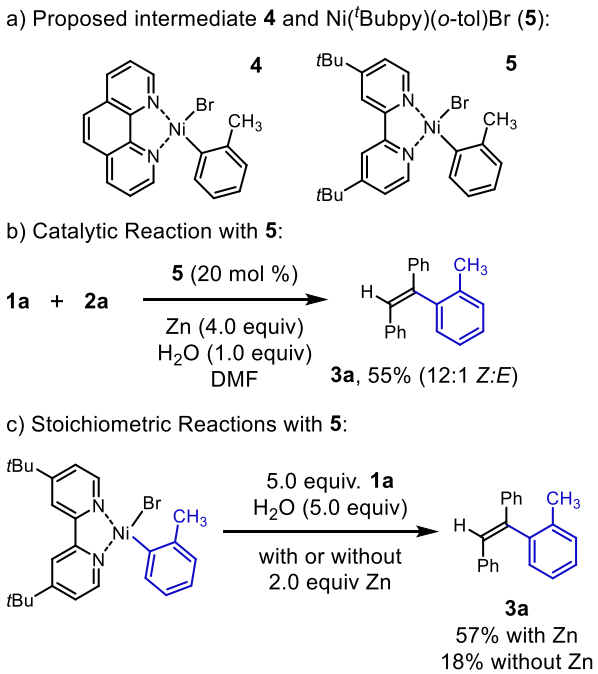
Based on the results of the aryl bromide substrate scope and our initial observations regarding optimization of the hydroarylation reaction, we began to test several different mechanistic hypotheses. Our initial assumption was that the hydrogen atom incorporated in the alkene product was derived from water, although reactions with freshly distilled DMF always yielded product. We believe that Ni–C bond homolysis and hydrogen atom abstraction are responsible for the substantial background reaction observed when exogenous H_2O is omitted. Indeed, when the hydroarylation reaction was performed with 3.0 equiv D_2O, the product was isolated in a 59% yield with 81% deuterium incorporation (Scheme 3). Reactions employing 1.0 equiv D_2O were lower yielding. When 1.0 equiv H_2O was used with d_7-DMF as the solvent, no deuterium incorporation could be measured. When both D_2O and d_7-DMF were used, the level of deuterium incorporation remained unchanged relative to the experiment with D_2O and DMF. Reactions performed in d_7-DMF with no H_2O or D_2O showed no deuterium incorporation. We believe these observations are consistent with a protonolysis step in the catalytic cycle when H_2O is present. Since the solvent (DMF) is not the additional source of hydrogen atoms, we posited that the benzylic C–H bonds present in the aryl bromide reactants could be the donors. In the place of deuterated aryl halide, we employed 5.0 equiv d_8-toluene as an additive and substitute C–D donor. This experiment provided 87% deuterium incorporation in the final product. This observation may help to explain why more than 1.0 equiv of the aryl bromide is required for adequate chemical yield and why reactions omitting water produce more byproducts.[26] Presumably, the alkene products could also become sacrificial C–H donors in the absence of water or excess aryl bromide. This may be an important consideration in other Ni-catalyzed reductive coupling reactions since hydrodehalogenation often contributes to byproduct formation.[19,27] We believe this method could be useful for applications such as drug development since an isotopic label can be incorporated under mild conditions using a relatively inexpensive donor (D_2O).

Scheme 3. Deuterium-Labeling Experiments

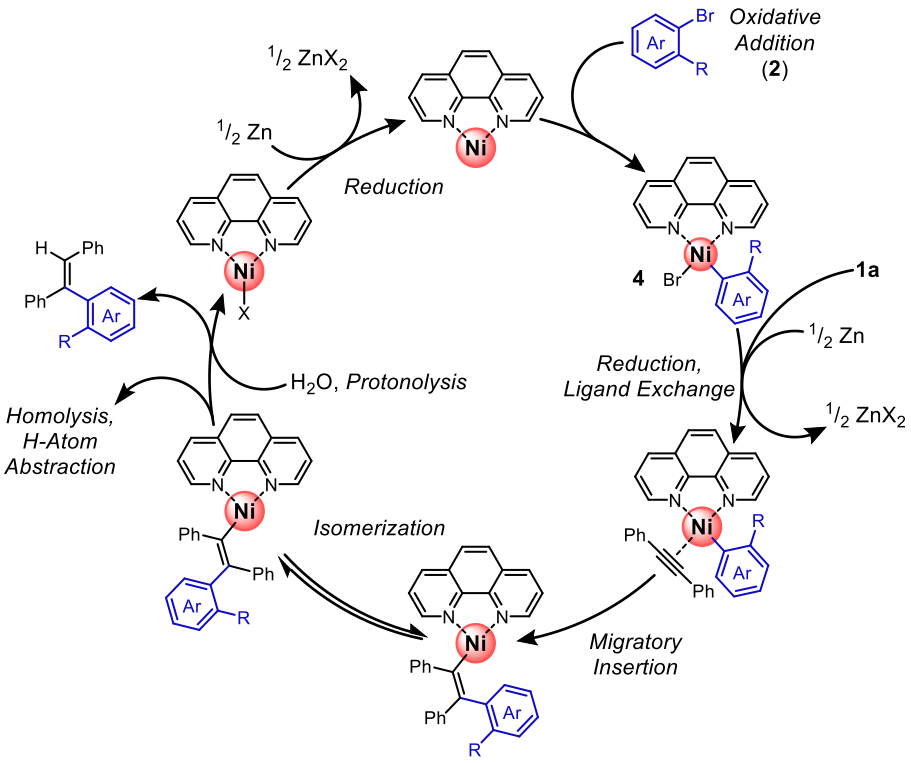


In accordance with other Ni-catalyzed reductive coupling reactions, we hypothesized that a Ni(II) aryl halide complex was an active catalytic intermediate.[18,19] We were, however, unable to synthesize the Ni(II) aryl halide complex **4** (Scheme 4a). We eventually settled on mechanistic studies with the known complex Ni(ᵗBubpy)(*o*-tol)Br (**5**)[20c] since Ni(ᵗBubpy)Cl_2 was also an active precatalyst for the hydroarylation reaction (Table 1, 46%, 12:1 *Z*/*E*). Hydroarylation reactions prepared with a 20 mol % loading of **5** provided **3a** in a 55% yield (Scheme 4b). This supports the hypothesis that a species such as **4** is likely on the catalytic cycle when Ni(phen)Cl_2 is used as a precatalyst.

Scheme 4. Experiments with Ni(ᵗBubpy)(*o*-tol)Br (5)



Scheme 5. Proposed Mechanism for the Ni-Catalyzed Alkyne Hydroarylation Reaction



Lastly, we set out to ascertain whether migratory insertion and protonolysis occur from the Ni(II) or Ni(I) oxidation state during hydroarylation. Since the hydroarylation reaction is performed under reductive conditions with Zn, either oxidation state could be involved. A stoichiometric reaction between **5**, **1a** (5.0 equiv), H_2O (5.0 equiv), and Zn (2.0 equiv) provided **3a** in a 57% yield, while an identical control reaction that excluded Zn produced an 18% yield for the alkene (Scheme 4c). We believe these experiments provide evidence that after oxidative addition with the aryl bromide, reduction must occur, and at least one of the subsequent intermediates reacts through the Ni(I) oxidation state. The non-negligible yield for **3a** observed when Zn is excluded may be due to a slower reaction from the Ni(II) oxidation state, or it could be due to an active Ni(I) species generated by an alternative mechanism. Jamison and coworkers have reported a mechanism for the reduction of Ni(II) aryl halide precatalysts that occurs without exogenous reductant under conditions which facilitate halide abstraction.[28] Presumably, a similar mechanism may lead to a catalytically active Ni(I) species here as well. This process could involve the disproportionation of **4** to yield a Ni(II) species with two aryl ligands. Subsequent reductive elimination to give a Ni(0) complex and reaction with another equivalent of **4** would provide a Ni(I) species.

Building on our observations, we have proposed a tentative mechanism for this Ni-catalyzed hydroarylation reaction (Scheme 5). The Ni(II) precatalyst can be reduced to the Ni(0) oxidation state by Zn, and then oxidative addition with the aryl bromide would produce a species equivalent to **4**. A reaction prepared with 3.0 equiv of a preformed arylzinc reagent provided the product in a low yield (~10%). Control experiments lacking the Ni precatalyst produce no hydroarylation products, no conversion of either organic reactant, and most importantly, no hydrodehalogenation products. These observations indicate that the direct involvement of an arylzinc reagent is not likely since Zn does not undergo insertion with the aryl bromide substrates under these conditions.[29] We believe **4** is reduced by Zn to give a Ni(I) complex which can undergo subsequent alkyne coordination, migratory insertion, isomerization, and protonolysis.[30] Catalyst turnover would occur through reduction by Zn.

We propose that isomerization of a vinyl Ni species is responsible for the *anti* selectivity observed in this reaction. The *syn* selectivity of migratory insertion is well established, and presumably a (*Z*) vinyl Ni intermediate would be initially formed by this step. Protonolysis of Ni–C bonds is generally regarded to occur with retention of configuration.[31] Equilibration of the (*Z*) vinyl Ni isomer with the (*E*) isomer prior to protonolysis would give the net effect of an *anti*-selective hydroarylation congruent with the experimental details listed above. When both isomers of alkene **3m** are separated and resubmitted to identical reaction conditions with Ni precatalyst, Zn, H_2O, and a different aryl bromide (**2a**), they are recovered without isomerization. The formation of **3a** from **2a** is not impeded in those reactions. The observation of semireduction products during reaction optimization would imply that Ni hydride species can be formed in the presence of Zn and H_2O. A Ni hydride species could presumably isomerize the alkene products via reversible hydrometalation, and that could alter the observed stereochemistry, but that does not appear to be the case under the conditions listed above.

Vinyl Ni intermediates have demonstrated competitive isomerization of the C=C double bond in previous examples.[32] Numerous mechanisms have been proposed for this isomerization, including nucleophilic attack on the C=C bond by free ligand,[32a,b] rapid Ni–C bond homolysis and recombination,[11b] and unimolecular rotation of the vinyl Ni C=C bond.[32a] The deuterium-labeling experiments summarized above imply that Ni–C bond homolysis occurs to some extent under the reaction conditions. It is not clear, however, if this process is reversible, or if it contributes to isomerization before protonolysis. Direct unimolecular rotation of the vinyl Ni C=C bond cannot be ruled out as a potential mechanism for isomerization. Mesomeric donation by a metal center has been proposed to facilitate direct unimolecular isomerization in a related vinyl Pd species.[33] This suggests that a vinyl Ni species with a carbene-like structure may facilitate the direct unimolecular isomerization process and that the specific oxidation state at Ni could influence both the rate and position of equilibrium during isomerization. It is noteworthy that other protic donors such as methanol, ethanol, isopropanol, and *tert*-butanol all give similar diastereoselectivities compared to water, suggesting that isomerization is rapid, and the rate of protonolysis does not influence the stereoselectivity. We believe a similar addition and isomerization mechanism likely drives the *anti* selectivity observed by Hartwig and Robbins.[17,34]

In conclusion, we have reported an *anti*-selective hydroarylation reaction which uses straightforward procedures and inexpensive reagents and precatalysts. Convincing mechanistic evidence is provided along with an initial substrate scope. Current investigations are focused on improving the diastereoselectivity of this reaction and computational studies to elucidate the mechanism of isomerization.

Experimental Section

General Information. DMF was distilled from CaH_2 and stored in a N_2-filled glovebox with molecular sieves. DMF could also be dried by sparging with Ar and passing through activated alumina (decagram-scale synthesis of **3a**). The effects of using DMF which was not rigorously dried or purified for the title reaction are presented above (Table 1). Reagents were purchased from Fisher Scientific, Acros Organics, Sigma-Aldrich, or Alfa Aesar and used as received. Aryl halides appearing in this study were used as received or filtered through a plug of silica gel and sparged with N_2 before handling in the glovebox. The precatalysts Ni(phen)Cl_2, Ni(phen)Br_2, Ni(bpy)Cl_2, and Ni(^{t}Bubpy)Cl_2 were synthesized according to previous literature procedures.[35] Granular Zn (20-40 mesh) was used for the hydroarylation reactions. For comparisons with different Zn sources, see the supporting information. Thin-layer chromatography (TLC) was performed on Al foil silica gel plates purchased from Sigma-Aldrich. Infrared spectra were obtained on a Thermo Scientific Nicolet iS10 infrared spectrometer. Gas chromatography-mass spectrometry (GC-MS) analysis was performed on a Trace 1310 gas chromatograph equipped with an ISQ mass spectrometer. Nuclear magnetic resonance (NMR) analysis (^{1}H and ^{13}C) was performed on a Bruker Avance III HD 850 MHz NMR spectrometer equipped with a TCI Cryoprobe, a Bruker Avance III HD 600 MHz NMR spectrometer equipped with a TCI Cryoprobe, or a Bruker Avance III HD 500 NMR spectrometer equipped with a TBI probe. Chemical shifts are reported in parts per million downfield from tetramethylsilane and are referenced to solvent signals (^{1}H NMR: $CHCl_3$ at 7.27 ppm; $(CD_3)_2CO$ at 2.05 and ^{13}C NMR: $CDCl_3$ at 77.0 ppm). NMR data are represented as follows: chemical shift (δ) (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration (H)).

General Procedure A for Reaction Optimization and GC-MS Analysis. Outside of a glovebox, a 2 dram scintillation vial was charged with a magnetic stir bar, diphenylacetylene (**1a**, 85 mg, 0.477 mmol, 1.0 equiv), Ni(phen)Cl_2 (29.6 mg, 0.0955 mmol, 20 mol %), and Zn (125 mg, 1.91 mmol, 4.0 equiv). The vial was transferred into a N_2-filled glovebox. The solvent (DMF, 5 mL) and *ortho*-bromotoluene (**2a**, 170 µL, 1.41 mmol, 3.0 equiv) were added via syringe. The vial was sealed and removed from the glovebox. DI H_2O (8.6 µL, 0.477 mmol, 1.0 equiv, deoxygenated by sparging with N_2 for 5 minutes) was added under N_2 via syringe. The vial was placed in an aluminum heating mantle set to 70 °C, and stirred rapidly for 16 hours. The reaction was cooled to room temperature and carefully added to saturated aq NH_4Cl (5 mL). The aqueous mixture was extracted with DCM (3 x 5 mL), and each extraction was passed through a small silica gel plug and collected in a 20 mL scintillation vial. The internal standard (*para*-xylene, 50 µL, 0.4055 mmol) was added via syringe. A 1 µL aliquot was removed from the vial, diluted with DCM (0.5-2.0 mL), and analyzed by GC-MS. Yields reported by GC-MS have been corrected using relative response factors which were calculated by analyzing a known mass of the purified product with the internal standard added. The entries 2-15 in Table 1 represent changes to these general conditions. For images of the experimental setup, and a representative crude GC-MS chromatogram, refer to the supporting information.

General Procedure B for Large Scale Reactions and Isolated Yields. A 25 mL round bottom flask was charged with a magnetic stir bar, alkyne **1** (1.12 mmol, 1.0 equiv), Ni(phen)Cl_2 (69.5 mg, 0.224 mmol, 20 mol %), and Zn (293 mg, 4.48 mmol, 4.0 equiv). The flask was transferred into a N_2-filled glovebox. The solvent (DMF, 12 mL) and aryl bromide **2** (3.33 mmol, 3.0 equiv) were added via syringe. The flask was sealed with a rubber septum and removed from the glovebox. DI H_2O (20 µL, 1.11 mmol, 1.0 equiv, deoxygenated) was added via syringe. The flask was placed in an oil bath previously heated to 70 °C and stirred for 16-24 hours. The reaction was allowed to cool to room temperature, quenched with aq NH_4Cl (20 mL), and then extracted with ethyl acetate (3 x 20 mL). The organic fractions were washed with DI H_2O (2 x 60 mL) and brine (1 x 60 mL), dried with anhydrous Na_2SO_4, and concentrated via rotary evaporation. The product was isolated after column chromatography on silica gel using hexanes as the eluent unless otherwise noted. For images of the experimental setup, refer to the supporting information.

*(1-(o-Tolyl)ethene-1,2-diyl)dibenzene (**3a**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 2-bromotulene (**2a**, 400 µL, 3.33 mmol). The *Z*/*E* ratio was determined to be 8.2:1 by ^{1}H NMR. The compound was isolated as a clear oil (214 mg, 0.791 mmol, 71%). The analytical data matched that reported in the literature:[17,36] ^{1}H NMR (850 MHz, $CDCl_3$, major diastereomer) δ 7.35-7.30 (m, 4H), 7.30-7.25 (m, 3H), 7.25-7.20 (m, 1H), 7.15-7.10 (m, 4H), 7.09 (s, 1H), 6.99-6.95 (m, 2H), 2.08 (s, 3H).

*Ethene-1,1,2-triyltribenzene (**3b**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and bromobenzene (**2b**, 355 μL, 3.37 mmol). The compound was isolated as a clear oil (187 mg, 0.728 mmol, 65%). The analytical data matched that reported in the literature:[37] ^{1}H NMR (850 MHz, $CDCl_3$,) δ 7.37-7.31 (m, 7H), 7.30-7.28 (t, *J* = 6.8 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.16-7.10 (m, 3H), 7.05 (d, *J* = 6.8 Hz, 2H), 6.99 (s, 1H).

*(1-(p-Tolyl)ethene-1,2-diyl)dibenzene (**3c**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-4-methylbenzene (**2c**, 576 mg, 3.37 mmol). The *Z/E* ratio was determined to be 1:1 by ^{1}H NMR. The compound was isolated as a clear oil (164 mg, 0.607 mmol, 54%)**.** The analytical data matched that reported in the literature:[38] ^{1}H NMR (600 MHz, $CDCl_3$, (*E*) diastereomer) δ 7.43-7.31 (m, 4H), 7.30-7.26 (m, 2H), 7.22-7.14 (m, 6H), 7.13-7.11 (m, 1H), 7.10-7.06 (m, 1H), 6.99 (s, 1H), 2.42, (s, 3H); characteristic peaks of (*Z*) diastereomer: δ 7.01 (s, 1H, alkene H), 2.44 (s, 3H, methyl).

*(1-(4-Methoxyphenyl)ethene-1,2-diyl)dibenzene (**3d**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 4-bromoanisole (**2d**, 420 μL, 3.35 mmol).The *Z/E* ratio was determined to be 1:1 by ^{1}H NMR. The compound was isolated as a clear oil using 10% ethyl acetate/hexanes as the chromatography eluent (192 mg, 0.670 mmol, 60%). The analytical data matched that reported in the literature:[39] ^{1}H NMR (500 MHz, $CDCl_3$, (*E*) and (*Z*) diastereomers) δ 7.37-7.27 (m, 5H), 7.25-7.21 (m, 1H), 7.18-7.08 (m, 5H), 7.05-7.01 (m, 1H), 6.93, 6.92 (s, 1H), 6.91-6.85 (m, 2H) 3.86, 3.84 (s, 3H).

*(1-(4-Chlorophenyl)ethene-1,2-diyl)dibenzene (**3e**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-4-chlorobenzene (**2e**, 394 μL, 3.36 mmol). The *Z/E* ratio was determined to be 1:1 by ^{1}H NMR. The compound was isolated as a clear oil (136 mg, 0.468 mmol, 42%). The analytical data matched that reported in the literature:[39] ^{1}H NMR (850 MHz, $CDCl_3$, (*E*) and (*Z*) diastereomers) δ 7.38-7.27 (m, 7H), 7.24-7.14 (m, 5H), 7.07 (d, *J* = 7.3 Hz, 2H, (*Z*) diastereomer), 7.05 (d, *J* = 7.0 Hz, 2H, (*E*) diastereomer), 7.00 (s, 1H, (*Z*) diastereomer), 6.98 (s, 1H, (*E*) diastereomer).

*(1-(4-Fluorophenyl)ethene-1,2-diyl)dibenzene (**3f**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-4-fluorobenzene (**2f**, 370 μL, 3.36 mmol). The *Z/E* ratio was determined to be 1:1 by ^{1}H NMR. The compound was isolated as a clear oil (200 mg, 0.729 mmol, 65%). The analytical data matched that reported in the literature:[39] ^{1}H NMR (850 MHz, $CDCl_3$, (*E*) and (*Z*) diastereomers) δ 7.38-7.29 (m, 5H), 7.23-7.11 (m, 5H), 7.08-7.00 (m, 4H), 6.99 (s, 1H, (*Z*) diastereomers), 6.94 (s, 1H, (*E*) diastereomers).

*(1-(4-(Trifluoromethyl)phenyl)ethene-1,2-diyl)dibenzene (**3g**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 4-bromobenzotrifluoride (**2g**, 471 μL, 3.36 mmol). The *Z/E* ratio was determined to be 1:1 by ^{1}H NMR. The compound was isolated as a clear oil (205 mg, 0.632 mmol, 56%). The analytical data matched that reported in the literature:[39] ^{1}H NMR (850 MHz, $CDCl_3$, (*E*) and (*Z*) diastereomers) δ 7.64-7.57 (m, 2H), 7.47-7.30 (m, 6H), 7.23-7.15 (m, 4H), 7.10-7.02 (m, 3H).

*Methyl 4-(1,2-diphenylvinyl)benzoate (**3h**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and methyl 4-bromobenzoate (**2h**, 483 μL, 3.36 mmol). The *Z/E* ratio was determined to be 1:1 by ^{1}H NMR. The compound was isolated as a clear oil using 10% ethyl acetate/hexanes as the chromatography eluent (250 mg, 0.795 mmol, 71%). The analytical data matched that reported in the literature:[10d] ^{1}H NMR (850 MHz, $CDCl_3$, (*E*) and (*Z*) diastereomers) δ 8.04 (d, *J* = 8.4 Hz, 2H, (*Z*) diastereomer), 8.00 (d, *J* = 8.6 Hz, 2H, (*E*) diastereomer),7.45-7.30 (m, 6H), 7.24-7.22 (m, 1H), 7.20-7.15 (m, 3H), 7.09-7.04 (m, 3H), 3.96 (s, 3H, (*Z*) diastereomer), 3.95 (s, 3H, (*E*) diastereomer).

*(1-(2,4-Dimethylphenyl)ethene-1,2-diyl)dibenzene (**3i**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-2,4-dimethylbenzene (**2i**, 455 μL, 3.37 mmol). The *Z/E* ratio was determined to be 7.0:1 by ^{1}H NMR. The compound was isolated as a clear oil (193 mg, 0.679 mmol, 61%). The analytical data matched that reported in the literature:[10c] ^{1}H NMR (600 MHz, $CDCl_3$, major diastereomer) δ 7.39-7.23 (m, 4H), 7.31-7.27 (m, 1H), 7.25-7.13 (m, 4H), 7.10 (s, 1H alkene H, (*Z*) diastereomer), 7.08-7.04 (m, 2H), 7.03-7.01 (m, 2H), 2.05 (s, 3H), 2.12 (s, 3H); characteristic peaks of (*E*) diastereomer: δ 6.65 (s, 1H, alkene H), 2.38 (s, 3H, methyl), 2.13 (s, 3H, methyl).

*(1-(2,5-Dimethylphenyl)ethene-1,2-diyl)dibenzene (**3j**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 2-bromo-1,4-dimethylbenzene (**2j**, 465 μL, 3.37 mmol). The *Z/E* ratio was determined to be 4.1:1 by ^{1}H NMR. The compound was isolated as a clear oil (230 mg, 0.809 mmol, 72%). The analytical data matched that reported in the literature:[40] ^{1}H NMR (600 MHz, $CDCl_3$, major diastereomer) δ 7.45-7.41 (m, 2H), 7.40-7.37 (m, 2H), 7.36-7.32 (m, 1H), 7.27-7.18 (m, 6H), 7.14 (s, 1H), 7.08-7.05 (m, 2H), 2.37, (s, 3H), 2.10 (s, 3H); characteristic peaks of minor diastereomer: δ 6.70 (s, 1H, alkene H), 2.42 (s, 3H, methyl), 2.17 (s, 3H, methyl).

*(1-(2,3-Dimethylphenyl)ethene-1,2-diyl)dibenzene (**3k**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-2,3-dimethylbenzene (**2k**, 456 μL, 3.36 mmol).The *Z/E* ratio was determined to be 5.0:1 by ^{1}H NMR. For detailed experiments supporting the stereochemical assignment, refer to the supporting information. The compound was isolated as a clear oil (193 mg, 0.679 mmol, 60%). The analytical data: ^{1}H NMR (600 MHz, $CDCl_3$, major diastereomer) δ 7.40-7.26 (m, 5H), 7.25-7.12 (m, 6H), 7.11 (s, 1H), 7.03-6.98 (m, 2H), 2.34 (s, 3H), 2.02 (s, 3H); characteristic peaks of minor diastereomer: δ 6.63 (s, 1H, alkene CH), 2.31 (s, 3H, methyl), 2.15 (s, 3H, methyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, major diastereomer) δ 142.7, 142.0, 139.7, 137.43, 137.42, 135.0, 129.2, 129.1, 128.4, 128.11, 128.08, 127.9, 127.3, 126.8, 126.6, 126.1, 20.6, 16.2; minor diastereomer 144.3, 143.3, 140.5, 137.5, 137.2, 134.7, 130.0, 129.8, 129.4, 129.0, 128.2, 128.1, 128.0, 127.0, 126.7, 125.1, 20.6, 16.9 (one peak must have coincidental overlap with major diastereomer); IR (thin film, cm^{-1}) 3054, 3020, 2917, 1597, 1490, 1470, 1446, 1382; HRMS (APPI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{21}$: 285.1638; Found: 285.1643.

*(1-(2-Ethylphenyl)ethene-1,2-diyl)dibenzene (**3l**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-2-ethylbenzene (**2l**, 466 μL, 3.37 mmol). The *Z/E* ratio was determined to be 6.3:1 by ^{1}H NMR. For detailed experiments supporting the stereochemical assignment, refer to the supporting information. The compound was isolated as a clear oil (181 mg, 0.638 mmol, 57%). The analytical data: ^{1}H NMR (600 MHz, $CDCl_3$, major diastereomer) δ 7.40-7.26 (m, 5H), 7.25-7.12 (m, 6H), 7.12 (s, 1H), 7.03-6.98 (m, 2H), 2.34 (s, 3H), 2.02 (s, 3H); characteristic peaks of minor diastereomer: δ 6.67 (s, 1H, alkene CH), 2.31 (s, 3H, methyl), 2.15 (s, 3H, methyl); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, major diastereomer) δ 142.7, 142.0, 139.7, 137.43, 137.42, 135.0, 129.2, 129.1, 128.4, 128.11, 128.08, 127.9, 127.3, 126.8, 126.6, 126.1, 20.6, 16.2; minor diastereomer 144.3, 143.3, 140.5, 137.5, 137.2, 134.7, 130.0, 129.8, 129.4, 129.0, 128.2, 128.1, 128.0, 127.0, 126.7, 125.1, 20.6, 16.9 (one peak must have coincidental overlap with major diastereomer); IR (thin film, cm^{-1}) 3054, 3020, 2917, 1597, 1490, 1470, 1446, 1382; HRMS (APPI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{21}$: 285.1638; Found: 285.1643.

*1-(1,2-Diphenylvinyl)naphthalene (**3m**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromonaphthalene (**2m**, 697 mg, 3.36 mmol). The *Z/E* ratio was determined to be 3.5:1 by ^{1}H NMR. The compound was isolated as a clear oil (178 mg, 0.581 mmol, 52%). The analytical data matched that reported in the literature:[41] ^{1}H NMR (600 MHz, $CDCl_3$, (*Z*) diastereomer) δ 7.97-7.89 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.60-7.35 (m, 10H), 7.08-7.00 (m, 3H), 6.94-6.88 (m, 2H); characteristic peaks of (*E*) diastereomer: δ 8.15 (d, *J* = 8.5 Hz, 1H), 6.81 (s, 1H).

*(1-(m-Tolyl)ethene-1,2-diyl)dibenzene (**3n**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-3-methylbenzene (**2n**, 408 μL, 3.36 mmol). The *Z/E* ratio was determined to be 1.2:1 by ^{1}H NMR. The compound was isolated as a clear oil (186 mg, 0.688 mmol, 61%). The analytical data matched that reported in the literature:[7e,36b] ^{1}H NMR (600 MHz, $CDCl_3$, (*E*) and (*Z*) diastereomers) δ 7.42-7.30 (m, 4H), 7.30-7.23 (m, 2H), 7.23-7.12 (m, 5H), 7.12-7.05 (m, 3H), 7.03-6.99 (m, 1H), 2.39 (s, 3H, (*Z*) diastereomer), 2.36 (s, 3H, (*E*) diastereomer).

*(1-(3-Ethylphenyl)ethene-1,2-diyl)dibenzene (**3o**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-3-ethylbenzene (**2o**, 357 μL, 2.60 mmol). The *Z/E* ratio was determined to be 1:1 by ^{1}H NMR. The compound was isolated as a clear oil (176 mg, 0.619 mmol, 55%). The analytical data matched that reported in the literature:[42] ^{1}H NMR (600 MHz, $CDCl_3$, (*E*) and (*Z*) diastereomers) δ 7.41-7.22 (m, 6H), 7.21-7.12 (m, 5H), 7.12-7.05 (m, 3H), 7.01 (s, 1H, alkene H, (*Z*) diastereomer), 6.99 (s, 1H, alkene H, (*E*) diastereomer), 2.68 (q, *J* = 7.6 Hz, 2H, single diastereomer), 2.62 (q, *J* = 7.6 Hz, 2H, single diastereomer), 1.27 (t, *J* = 7.6 Hz, 3H, (*E*) diastereomer), 1.19 (t, *J* = 7.6 Hz, 3H, (*Z*) diastereomer).

*(Z)-(1-(3,5-di-tert-butylphenyl)ethene-1,2-diyl)dibenzene (**3p**)*. The title compound was prepared according to the general procedure B using **1a** (200 mg, 1.12 mmol) and 1-bromo-3,5-di-*tert*-butylbenzene (**2p**, 906 mg, 3.36 mmol). The *Z/E* ratio was determined to be 1.4:1 by ^{1}H NMR. The compound was isolated as a clear oil (219 mg, 0.594 mmol, 53%). The analytical data matched that reported in the literature:[43] ^{1}H NMR (600 MHz, $CDCl_3$, (*E*) and (*Z*) diastereomers) δ 7.41-7.22 (m, 6H), 7.21-7.12 (m, 5H), 7.12-7.05 (m, 3H), 7.01 (s, 1H, alkene H, (*Z*) diastereomer), 6.99 (s, 1H, alkene H, (*E*) diastereomer), 2.68 (q, *J* = 7.6 Hz, 2H, single diastereomer), 2.62 (q, *J* = 7.6 Hz, 2H, single diastereomer), 1.27 (t, *J* = 7.6 Hz, 3H, (*E*) diastereomer), 1.19 (t, *J* = 7.6 Hz, 3H, (*Z*) diastereomer).

*Trimethyl(2-phenyl-2-(o-tolyl)vinyl)silane (**3q**)*. The title compound was prepared according to the general procedure B using 1-phenyl-2-trimethylsilylacetylene (**1c**, 221 μL, 1.12 mmol) and 2-bromotulene (**2a**, 405 μL, 3.36 mmol). The *Z/E* ratio was determined to be >20:1 by ^{1}H NMR. For detailed experiments supporting the stereochemical assignment, including stereospecific chemical modification to a previously reported compound, refer to the supporting information. The compound was isolated as a clear oil (152 mg, 0.570 mmol, 51%). The analytical data: ^{1}H NMR (600 MHz, $CDCl_3$, (*Z*) diastereomer) δ 7.35-7.25 (m, 7H), 7.24-7.19 (m, 2H), 6.47 (s, 1H), 2.08 (s, 3H), -0.10 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, (*Z*) diastereomer) δ 156.3, 141.9, 141.5, 136.3, 130.4, 129.9, 129.0, 128.2, 127.5, 126.5, 126.2, 125.3, 19.6, 0.00; IR (thin film, cm^{-1}) 3059, 3018, 2952, 1585, 1567, 1492, 1444, 1332; HRMS (APPI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{22}Si$: 266.1491; Found: 266.1490.

General Procedure C for the Decagram-Scale Synthesis of 3a. Outside of a glovebox an oven-dried 1 L round bottom flask was charged with a magnetic stir bar, diphenylacetylene (**1a**, 10 g, 56.1 mmol, 1.0 equiv), Ni(phen)Cl_2 (3.48 g, 11.2 mmol, 20 mol %), and Zn (14.7 g, 225 mmol, 4.0 equiv). The flask was evacuated and refilled with N_2 several times. The solvent (DMF, 600 mL) was added under an inert atmosphere using a solvent dispensing system and then *ortho*-bromotoluene (**2a**, 20 mL, 169 mmol, 3.0 equiv) and DI H_2O (1.01 mL, 56.1 mmol, 1.0 equiv, deoxygenated) were added under N_2 via syringe. The round bottom flask was placed in an oil bath previously heated to 70 °C, and stirred under N_2 rapidly for 28 hours. The reaction was allowed to cool to room temperature, quenched with saturated aq NH_4Cl (400 mL), and stirred for several minutes. The aqueous mixture was filtered through a pad of Celite and divided into two even (500 mL) portions. Each 500 mL aqueous portion was extracted with diethyl ether (2 x 300 mL) in a 1 L separatory funnel. Each (300 mL) organic fraction was transferred to a 500 mL separatory funnel and washed with DI H_2O (2 x 100 mL) and brine (2 x 100 mL) to remove residual DMF (which hampers column chromatography). The organic solutions were then dried with anhydrous Na_2SO_4, transferred to a 500 mL round bottom flask, and concentrated sequentially via rotary evaporation. The *Z/E* ratio was determined by ^{1}H NMR of the crude reaction mixture (8.3:1 *Z/E*). The product was isolated after column chromatography on silica gel using hexanes as an eluent. Using general procedure C the compound **3a** was isolated as a clear oil (10.9 g, 40.3 mmol, 72%). The analytical data for **3a** synthesized using general procedure C was identical to that reported above. For images of the experimental setup, refer to the supporting information.

Deuterium-Labeling Experiments. Outside of a glovebox a 25 mL round bottom flask was charged with a magnetic stir bar, diphenylacetylene (**1a**, 200 mg, 1.12 mmol, 1.0 equiv), Ni(phen)Cl_2 (69.5 mg, 0.224 mmol, 20 mol %), and Zn (293

mg, 4.48 mmol, 4.0 equiv). The flask was then transferred into a N_2-filled glovebox. The solvent (DMF, 12 mL) and *ortho*-bromotoluene (**2a**, 400 µL, 3.33 mmol, 3.0 equiv) were added via syringe. The round bottom flask was sealed with a rubber septum and removed from the glovebox. D_2O (60 µL, 3.32 mmol, 3.0 equiv, deoxygenated) was added under N_2 via syringe. The round bottom flask was placed in an oil bath previously heated to 70 °C, and stirred rapidly for 20 hours. The reaction was allowed to cool to room temperature, quenched with aq NH_4Cl, extracted with ethyl acetate, dried with anhydrous Na_2SO_4, and concentrated via rotary evaporation (identical to general procedure B). The product was isolated after column chromatography on silica gel using hexanes as the eluent. The compound **3a** was isolated as a clear oil (179 mg, 0.662 mmol, 59%, 7.4:1 *Z/E*). The mass observed for this compound (271.21 m/z) by GC-MS and ^{1}H NMR analysis both indicated deuterium incorporation. The extent of deuterium incorporation was determined to be 67-78% by integration of the alkene peak relative to the other ^{1}H NMR signals. Mass spectrometry analysis indicated deuterium incorporation to be 81%. Subsequent experiments with d_7-DMF were prepared on the 0.196 mmol scale (35 mg **1a**) with 2 mL of solvent (due to the cost of d_7-DMF). The extent of deuterium incorporation was determined by mass spectrometry for those reactions.

Reactions with Ni(^{t}Bubpy)(*o*-tolyl)Br (5). The compound Ni(^{t}Bubpy)(*o*-tolyl)Br (**5**) was prepared according to the procedure reported by Doyle.[19c] The analytical data matched that reported in the literature:[19b,c] ^{1}H NMR (600 MHz, acetone-d_6) δ 9.26 (s, 1H), 8.42 (d, *J* = 22 Hz, 2H), 7.69 (s, 1H), 7.52 (s, 1H), 7.34 (S, 1H), 7.02 (s, 1H), 6.74-6.69 (m, 3H), 3.01 (s, 3H), 1.43 (s, 9H), 1.36 (s, 9H).

Catalytic Reaction with Ni(tBubpy)(o-tolyl)Br (5). Outside of a glovebox a 25 mL round bottom flask was charged with a magnetic stir bar, diphenylacetylene (**1a**, 150 mg, 0.842 mmol, 1.0 equiv), Ni(^{t}Bubpy)(*o*-tolyl)Br (**5**, 83.8 mg, 0.168 mmol, 20 mol %), and Zn (220 mg, 3.36 mmol, 4.0 equiv). The flask was then transferred into a N_2-filled glovebox. The solvent (DMF, 9 mL) and *ortho*-bromotoluene (**2a**, 304 µL, 2.52 mmol, 3.0 equiv) were added via syringe. The round bottom flask was sealed with a rubber septum and removed from the glovebox. DI H_2O (15 µL, 0.842 mmol, 1.0 equiv, deoxygenated) was added under N_2 via syringe. The flask was placed in an oil bath previously heated to 70 °C, and stirred rapidly for 21 hours. The reaction was allowed to cool to room temperature, quenched with aq NH_4Cl, extracted with ethyl acetate, dried with anhydrous Na_2SO_4, and concentrated via rotary evaporation (identical to general procedure B). The product was isolated after column chromatography on silica gel using hexanes as the eluent. The compound **3a** was isolated as a clear oil (124 mg, 0.459 mmol, 55%, 12:1 *Z/E*).

Stoichiometric Reaction with Ni(tBubpy)(o-tolyl)Br (5). Outside of a glovebox a 25 mL round bottom flask was charged with a magnetic stir bar, diphenylacetylene (**1a**, 89 mg, 0.500 mmol, 5.0 equiv), Ni(^{t}Bubpy)(*o*-tolyl)Br (**5**, 50 mg, 0.100 mmol, 1.0 equiv), and Zn (13 mg, 0.20 mmol, 2.0 equiv). The flask was then transferred into a N_2-filled glovebox. The solvent (DMF, 5.35 mL) was added via syringe. The round bottom flask was sealed with a rubber septum and removed from the glovebox. DI H_2O (3.6 µL, 0.200 mmol, 2.0 equiv, deoxygenated) was added under N_2 via syringe. The round bottom flask was placed in an oil bath previously heated to 70 °C, and stirred rapidly for 22 hours. An identical reaction lacking Zn was prepared alongside this reaction. That reaction (the "no Zn" control reaction) was treated in an otherwise identical fashion. Both reactions were allowed to cool to room temperature, quenched with aq NH_4Cl, extracted with DCM, and analyzed by GC-MS (identical to general procedure A). The yield for the reaction with Zn was 57% by GC-MS, and the yield for the reaction which excluded Zn was 18% by GC-MS.

ASSOCIATED CONTENT

Supporting Information.
This material is available free of charge via the Internet at http://pubs.acs.org.

Reaction optimization, mechanistic experiments, and spectral data for all compounds (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: dwilger@samford.edu

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for partial support of this research (PRF# 56605-UNI1**)**. NMR experiments were performed at the UAB Cancer Center High-Field NMR Facility supported by the NIH grants 1P30 CA-13148, 1S10 RR022994-01A1, and1P30 CA-13148. We would also like to thank the Howard College of Arts and Sciences and Samford University for partial support of this research.

REFERENCES

(1) The Shell Higher Olefin Process relies upon ethylene oligomerization with a homogeneous Ni catalyst. This technology is used to produce millions of tons of alkene products each year. For a recent historical perspective, see: Keim, W. Oligomerization of Ethylene to α-Olefins: Discovery and Development of the Shell Higher Olefin Process (SHOP). *Angew. Chem., Int. Ed.* **2013**, *52*, 12492-12496.

(2) Large quantities of functionalized alkenes are continuously being synthesized using Pd catalysts. Many alkene monomers such as vinyl acetate are produced using Pd catalysts with associated mechanisms analogous to the Wacker process. For selected examples, see: (a) Calaza, F.; Stacchiola, D.; Neurock, M.; Tysoe, W. T. Coverage Effects on the Palladium-Catalyzed Synthesis of Vinyl Acetate: Comparison between Theory and Experiment. *J. Am. Chem. Soc.* **2010**, *132*, 2202-2207. (b) Kragtem, D. D.; van Santen, R. A. A Spectroscopic Study of the Homogeneous Catalytic Conversion of Ethylene to Vinyl Acetate by Palladium Acetate. *Inorg. Chem.* **1999**, *38*, 331-339. (c) Stacchiola, D.; Calaza, F.; Burkholder, L.; Tysoe, W. T. Vinyl Acetate Formation by the Reaction of Ethylene with Acetate Species on Oxygen-Covered Pd(111). *J. Am. Chem. Soc.* **2004**, *126*, 15384-15385. Many Pd-catalyzed cross-coupling reactions have been successfully patented and industrialized for the large-scale synthesis of more functionally elaborate alkenes. For a review, see: (d) Corbet, J.-P.; Mignani, G. Selected Patented Cross-Coupling Reaction Technologies. *Chem. Rev.* **2006**, *106*, 2651-2710.

(3) For selected examples of Cr-catalyzed carbometalation reactions between alkynes and organomagnesium reagents, see: (a) Murakami, K.; Ohmiya, H.; Yorimitsu, H.; Oshima, K. Chromium-Catalyzed Arylmagnesiation of Alkynes. *Org. Lett.* **2007**, *9*, 1569-1571. (b) Yan, J.; Yoshikai, N. Phenanthrene Synthesis via Chromium-Catalyzed Annulation of 2-Biaryl Grignard Reagents and Alkynes. *Org. Lett.* **2017**, *19*, 6630-6633. (c) Yan, J.; Yoshikai, N. Chromium-catalyzed migratory arylmagnesiation of unactivated alkynes. *Org. Chem. Front.* **2017**, *4*, 1972-1975.

(4) For the Mn-catalyzed addition of Grignard reagents to alkynes, see: Yorimitsu, H.; Tang, J.; Okada, K.; Shinokubo, H.; Oshima, K. Manganese-catalyzed Phenylation of Acetylenic Compounds with a Phenyl Grignard Reagent. *Chem. Lett.* **1998**, *27*, 11-12.

(5) For selected examples of Fe-catalyzed carbometalation reactions between alkynes and organolithium and/or organomagnesium reagents, see: (a) Hojo, M.; Murakami, Y.; Aihara, H.; Sakuragi, R.; Baba, Y.; Hosomi, A. Iron-Catalyzed Regio- and Stereoselective Carbolithiation of Alkynes. *Angew. Chem., Int. Ed.* **2001**, *40*, 621-623. (b) Shirakawa, E.; Yamagami, T.; Kimura, T.; Yamaguchi, S.; Hayashi, T. Arylmagnesiation of Alkynes Catalyzed Cooperatively by Iron and Copper Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 17164-17165. (c) Zhang, D.; Ready, J. M. Iron-Catalyzed Carbometalation of Propargylic and Homopropargylic Alcohols. *J. Am. Chem. Soc.* **2006**, *128*, 15050-15051. (d) Yamagami, T.; Shintani, R.; Shirakawa, E.; Hayashi, T. Iron-Catalyzed Arylmagnesiation of Aryl(alkyl)acetylenes in the Presence of an N-Heterocyclic Carbene Ligand. *Org. Lett.* **2007**, *9*, 1045-1048. (e) Shirakawa, E.; Masui, S.; Narui, R.; Watabe, R.; Ikeda, D.; Hayashi, T. Iron-catalyzed aryl- and alkenyllithiation of alkynes and its application to benzosilole synthesis. *Chem. Commun.* **2011**, *47*, 9714-9716.

(6) For selected examples of Co-catalyzed carbometalation reactions between alkynes and organozinc reagents, see: (a) Yasui, H.; Nishikawa, T.; Yorimitsu, H.; Oshima, K. Cobalt-Catalyzed Allylzincations of Internal Alkynes. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1271-1274. (b) Murakami, K.; Yorimitsu, H.; Oshima, K. Cobalt-Catalyzed Arylzincation of Alkynes. *Org. Lett.* **2009**, *11*, 2373-2375. (c) Corpet, M.; Gosmini, C. Cobalt-catalysed synthesis of highly substituted styrene derivatives via arylzincation of alkynes. *Chem. Commun.* **2012**, *48*, 11561–11563. (d) Wu, J.; Yoshikai, N. Cobalt-Catalyzed Alkenylzincation of Unfunctionalized Alkynes. *Angew. Chem., Int. Ed.* **2016**, *55*, 336-340.

(7) For selected examples of Ni-catalyzed carbometalation reactions with alkynes, see: (a) Stüdemann, T.; Knochel, P. New Nickel-Catalyzed Carbozincation of Alkynes: A Short Synthesis of (*Z*)-Tamoxifen. *Angew. Chem., Int. Ed.* **1997**, *36*, 93-95. (b) Shirakawa, E.; Yamasaki, K.; Yoshida, H.; Hiyama, T. Nickel-Catalyzed Carbostannylation of Alkynes with Allyl-, Acyl-, and Alkynylstannanes: Stereoselective Synthesis of Trisubstituted Vinylstannanes. *J. Am. Chem. Soc.* **1999**, *121*, 10221-10222. (c) Suginome, M.; Shirakura, M.; Yamamoto, A. Nickel-Catalyzed Addition of Alkynylboranes to Alkynes. *J. Am. Chem. Soc.* **2006**, *128*, 14438-14439. (d) Murakami, K.; Ohmiya, H.; Yorimitsu, H.; Oshima, K. Nickel-catalyzed Carbometalation Reactions of [2-(1-Propynyl)phenyl]methanol with 1-Alkenylmagnesium Reagents. *Chem. Lett.* **2007**, *36*, 1066-1067. (e) Xue, F.; Zhao, J.; Hor, T. S. A. Ambient arylmagnesiation of alkynes catalysed by ligandless nickel(II). *Chem. Commun.* **2013**, *49*, 10121-10123. (f) Xue, F.; Zhao, J.; Hor, T. S. A.; Hayashi, T. Nickel-Catalyzed Three-Component Domino Reactions of Aryl Grignard Reagents, Alkynes, and Aryl Halides Producing Tetrasubstituted Alkenes. *J. Am. Chem. Soc.* **2015**, *137*, 3189-3192.

(8) For selected examples of Cu-catalyzed carbometalation reactions with alkynes, see: (a) Xie, M.; Huang, X. Carbomagnesiation of Acetylenic Sulfones Catalyzed by CuCN and its Application in the Stereoselective Synthesis of Polysubstituted Vinyl Sulfones. *Synlett* **2003**, 477-480. (b) Kortman, G. D.; Hull, K. L. Copper-Catalyzed Hydroarylation of Internal Alkynes: Highly Regio- and Diastereoselective Synthesis of 1,1-Diaryl, Trisubstituted Olefins. *ACS Catal.* **2017**, *7*, 6220-6224. (c) Nakamura, K.; Nishikata, T. Tandem Reactions Enable Trans- and Cis-Hydro-Tertiary-Alkylations Catalyzed by a Copper Salt. *ACS. Catal.* **2017**, *7*, 1049-1052.

(9) For selected examples of Rh-catalyzed carbometalation reactions between alkynes and arylboronic acids, see: (a) Hayashi, T.; Inoue, K.; Taniguchi, N.; Ogasawara, M. Rhodium-Catalyzed Hydroarylation of Alkynes with Arylboronic Acids: 1,4-Shift of Rhodium from 2-Aryl-1-alkenylrhodium to 2-Alkenylarylrhodium Intermediate. *J. Am. Chem. Soc.* **2001**, *123*, 9918-9919. (b) Lautens, M.; Yoshida, M. Regioselective Rhodium-Catalyzed Addition of Arylboronic Acids to Alkynes with a Pyridine-Substituted Water-Soluble Ligand. *Org. Lett.* **2002**, *4*, 123-125. (c) Zhang, W.; Liu, M.; Wu, H.; Ding, J.; Cheng, J. Phosphine-free rhodium-catalyzed hydroarylation of diaryl acetylenes with boronic acids. *Tetrahedron Lett.* **2008**, *49*, 5214–5216. (d) Schipper, D. J.; Hutchinson, M.; Fagnou K. Rhodium(III)-Catalyzed Intermolecular Hydroarylation of Alkynes. *J. Am. Chem. Soc.* **2010**, *132*, 6910-6911.

(10) For selected examples of Pd-catalyzed carbometalation reactions with alkynes, see: (a) Oda, H.; Morishita, M.; Fugami, K.; Sano, H.; Kosugi, M. A Novel Diarylation Reaction of Alkynes by Using Aryltributylstannane in the Presence of Palladium Catalyst. *Chem. Lett.* **1996**, *25*, 811-812. (b) Oh, C. H.; Jung, H. H.; Kim, K. S.; Kim, N. The Palladium-Catalyzed Addition of Organoboronic Acids to Alkynes. *Angew. Chem., Int. Ed.* **2003**, *42*, 805-808. (c) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Persiani, D. Palladium-Catalyzed Hydroarylation of Alkynes with Arenediazonium Salts. *Org. Lett.* **2008**, *10*, 1597-1600. (d) Rao, S.; Joy, M. N.; Prabhu, K. R. Employing Water as the Hydride Source in Synthesis: A Case Study of Diboron Mediated Alkyne Hydroarylation. *J. Org. Chem.* **2018**, *83*, 13707-13715.

(11) For a Co-catalyzed multicomponent coupling reaction which employs carbon dioxide in conjunction with Zn as a reductant, see: (a) Nogi, K.; Fujihara, T.; Terao, J.; Tsuji, Y. Carboxyzincation Employing Carbon Dioxide and Zinc Powder: Cobalt-Catalyzed Multicomponent Coupling Reactions with Alkynes. *J. Am. Chem. Soc.* **2016**, *138*, 5547-5550. For examples of Ni-catalyzed reductive coupling reactions which employ carbon dioxide, see: (b) Wang, X.; Liu, Y.; Martin, R. Ni-Catalyzed Divergent Cyclization/Carboxylation of Unactivated Primary and Secondary Alkyl Halides with CO_2. *J. Am. Chem. Soc.* **2015**, *137*, 6476-6479. (c) Gaydou, M.; Moragas, T.; Juliá-Hernández, F.; Martin, R. Site-Selective Catalytic Carboxylation of Unsaturated Hydrocarbons with CO_2 and Water. *J. Am. Chem. Soc.* **2017**, *139*, 12161-12164.

(12) For a Ni-catalyzed multicomponent coupling reaction which employs aryl iodides in conjunction with Mn as a reductant, see: Dorn, S. C. M.; Olsen, A. K.; Kelemen, R. E.; Shrestha, R.; Weix, D. J. Nickel-catalyzed reductive arylation of activated alkynes with aryl iodides. *Tetrahedron Lett.* **2015**, *56*, 3365-3367. This reference also serves as an example for Ni-catalyzed alkyne hydroarylation with *syn* selectivity.

(13) For selected reviews discussing alkyne hydroarylation via transition-metal-catalyzed C–H activation, see: (a) Kakiuchi, F.; Murai, S. Catalytic C-H/Olefin Coupling. *Acc. Chem. Res.* **2002,** *35*, 826-834. (b) Gao, K.; Yoshikai, N. Low-Valent Cobalt Catalysis: New Opportunities for C−H Functionalization *Acc. Chem. Res.* **2014**, *47*, 1208−1219. (c) Sambiago, C.; Schönbauer, D.; Blieck, R.; Dao-Huy, T.; Pototschnig, G.; Schaaf, P.; Wiesinger, T.; Zia, M. F.; Wencel-Delord, J.; Besset, T.; Maes, B. U. W.; Schnürch, M. A comprehensive overview of directing groups applied in metal-catalysed C–H functionalization chemistry. *Chem. Soc. Rev.* **2018**, *47*, 6603-6743.

(14) For additional examples of Ni-catalyzed three-component couplings reactions involving alkynes, see: (a) Ogata, K.; Atsuumi, Y.; Fukuzawa, S.-i. Highly Chemoselective Nickel-Catalyzed Three-Component Cross-Trimerization between Two Distinct Terminal Alkynes and an Internal Alkyne. *Org. Lett.* **2011**, *13*, 122–125. (b) Li, Z.; García-Domínguez, A.; Nevado, C. Nickel-Catalyzed Stereoselective Dicarbofunctionalization of Alkynes. *Angew. Chem., Int. Ed.* **2016**, *55*, 6938-6941. (c) Shimada, Y.; Ikeda, Z.; Matsubara, S. Preparation of Organozinc Reagents via Catalyst Controlled Three-Component Coupling between Alkyne, Iodoarene, and Bis(iodozincio)methane. *Org. Lett.* **2017**, *19*, 3335–3337.

(15) (a) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. Efficient activation of aromatic C-H bonds for addition to C-

C multiple bonds. *Science* **2000**, *287*, 1992-1995. (b) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M; Fujiwara, Y. Novel Pd(II)- and Pt(II)-Catalyzed Regio- and Stereoselective *trans*-Hydroarylation of Alkynes by Simple Arenes. *J. Am. Chem. Soc*. **2000**, *122*, 7252-7263. (c) Jia, C.; Kitamura, T.; Fujiwara, Y. Catalytic Functionalization of Arenes and Alkanes via C−H Bond Activation. *Acc. Chem. Res.* **2001**, *34*, 633-639. (d) Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. N-heterocyclic carbene palladium complexes bearing carboxylate ligands and their catalytic activity in the hydroarylation of alkynes. *Organometallics* **2004,** *23*, 3752-3755.

(16) Shirakawa, E.; Takahashi, G.; Tsuchimoto, T.; Kawakami, Y. Nickel-catalysed hydroarylation of alkynes using arylboron compounds: selective synthesis of multisubstituted arylalkenes and aryldienes. *Chem. Commun*. **2001**, 2688-2689.

(17) Robbins, D. W.; Hartwig, J. F. A simple, multidimensional approach to high-throughput discovery of catalytic reactions. *Science* **2011**, *333*, 1423-1427.

(18) For reviews of Ni-catalyzed C–C bond-forming reactions, see: (a) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. Recent advances in homogeneous nickel catalysis. *Nature* **2014**, *509*, 299-309. (b) Ananikov, V. P. Nickel: The "Spirited Horse" of Transition Metal Catalysis. *ACS Catal.* **2015**, *5*, 1964-1971. (c) Huang, C.-Y.; Doyle, A. G. Electron-Deficient Olefin Ligands Enable Generation of Quaternary Carbons by Ni-Catalyzed Cross-Coupling. *J. Am. Chem. Soc.* **2015**, *137*, 5638−5641. (d) Choi, J.; Fu, G. C. Transition metal-catalyzed alkyl-alkyl bond formation: Another dimension in cross-coupling chemistry. *Science* **2017**, *356*, 152.

(19) For examples of Ni-catalyzed cross-coupling reactions performed under reductive conditions, see: (a) Montgomery, J. Nickel-Catalyzed Reductive Cyclizations and Couplings. *Angew. Chem., Int. Ed.* **2004**, *43*, 3890-3908. (b) Weix, D. J. Methods and Mechanisms for Cross-Electrophile Coupling of Csp^2 Halides with Alkyl Electrophiles. *Acc. Chem. Res.* **2015**, *48*, 1767-1775. (c) Arendt, K. M.; Doyle, A. G. Dialkyl Ether Formation by Nickel-Catalyzed Cross-Coupling of Acetals and Aryl Iodides. *Angew. Chem., Int. Ed.* **2015**, *54*, 9876-9880. (d) Woods, B. P.; Orlandi, M.; Huang, C.-Y.; Sigman, M. S.; Doyle, A. G. Nickel-Catalyzed Enantioselective Reductive Cross-Coupling of Styrenyl Aziridines. *J. Am. Chem. Soc.* **2017**, *139*, 5688-5691. (e) Heinz, C.; Lutz, J. P.; Simmons, E. M.; Miller, M. M.; Ewing, W. R.; Doyle, A. G. Ni-Catalyzed Carbon–Carbon Bond-Forming Reductive Amination. *J. Am. Chem. Soc.* **2018**, *140*, 2292-2300.

(20) For methods to synthesis Ni(II) aryl halide complexes with bipyridyl ligands, see: (a) Shields, B. J.; Doyle, A. G. Direct C(sp3)-H Cross Coupling Enabled by Catalytic Generation of Chlorine Radicals. *J. Am. Chem. Soc.* **2016**, *138*, 12719-12722. (b) Primer, D. N.; Molander, G. A. Enabling the Cross-Coupling of Tertiary Organoboron Nucleophiles through Radical-Mediated Alkyl Transfer. *J. Am. Chem. Soc*. **2017**, *139*, 9847-9850. (c) Shields, B. J.; Kudisch, B.; Scholes, G. D.; Doyle, A. G. Long-Lived Charge-Transfer States of Nickel(II) Aryl Halide Complexes Facilitate Bimolecular Photoinduced Electron Transfer. *J. Am. Chem. Soc.* **2018**, *140*, 3035−3039.

(21) The *supporting information* provides chemical yield comparisons for different substrates examined at both the 20% and 10% precatalyst loading.

(22) Reactions with both $Ni(phen)Cl_2$ and $Ni(phen)Br_2$ show an induction period before catalysis begins. Neither precatalyst is highly soluble in DMF and differences between the two are most likely due to differences in solubility and their initial reduction be Zn.

(23) For direct comparisons between the two different (10 and 20 mol %) precatalyst loadings, see the *supporting information*.

(24) (a) Trost, B. M.; Sorum, M. T.; Chan, C.; Rühter, G. Palladium-Catalyzed Additions of Terminal Alkynes to Acceptor Alkynes. *J. Am. Chem. Soc.* **1997**, *119*, 698-708. (b) Wang, X.; Nakajima, M.; Serrano, E.; Martin, R. Alkyl Bromides as Mild Hydride Sources in Ni-Catalyzed Hydroamidation of Alkynes with Isocyanates. *J. Am. Chem. Soc.* **2016**, *138*, 15531-15534. (c) Go, S. Y.; Lee, G. S.; Hong, S. H. Highly Regioselective and *E/Z*-Selective Hydroalkylation of Ynone, Ynoate, and Ynamide via Photoredox Mediated Ni/Ir Dual Catalysis. *Org. Lett.* **2018**, *20*, 4691-4694.

(25) Kong, W.; Che, C.; Wu, J.; Ma, L.; Zhu, G. Pd-Catalyzed Regio- and Stereoselective Addition of Boronic Acids to Silylacetylenes: A Stereodivergent Assembly of β,β-Disubstituted Alkenylsilanes and Alkenyl Halides. *J. Org. Chem.* **2014**, *79*, 5799-5805.

(26) When a hydroarylation reaction is prepared with **1a**, bromobenzene (**2b**), and 1.0 equiv D_2O the product (**3b**) showed a high degree of deuterium incorporation, but the yield was lower and numerous byproducts were formed. The extent of deuterium incorporation could not be measured in this case.

(27) Ackerman, L. K. G.; Lovell, M.; Weix, D. J. Multimetallic catalysed cross-coupling of aryl bromides with aryl triflates. *Nature* **2015**, *524*, 454-457.

(28) (a) Standley, E. A.; Jamison, T. F. Simplifying Nickel(0) Catalysis: An Air-Stable Nickel Precatalyst for the Internally Selective Benzylation of Terminal Alkenes. *J. Am. Chem. Soc*. **2013**, *135*, 1585−1592. (b) Standley, E. A.; Smith, S. J.; Müller, P.; Jamison, T. F. A Broadly Applicable Strategy for Entry into Homogeneous Nickel(0) Catalysts from Air-Stable Nickel(II) Complexes. *Organometallics* **2014**, *33*, 2012-2018.

(29) It is possible that one of the vinyl Ni intermediates undergoes transmetalation to Zn prior to protonolysis.

(30) Electrochemical studies are consistent with Zn being able to reduce a Ni(II) aryl halide complex to a Ni(I) aryl complex and these species are known to be active in C–C bond forming reactions: Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. Nickel-catalyzed cross-couplings involving carbon-oxygen bonds. *Chem. Rev*. **2011**, *111*, 1346-1416.

(31) Babu, M. H.; Kumar, G. R.; Kant, R.; Reddy, M. S. Ni-Catalyzed regio- and stereoselective addition of arylboronic acids to terminal alkynes with a directing group tether. *Chem. Commun*. **2017**, *53*, 3894-3897.

(32) (a) Huggins, J. M.; Bergman, R. G. Reaction of Alkynes with a Methylnickel Complex: Observation of a cis Insertion Mechanism Capable of Giving Kinetically Controlled trans Products. *J. Am. Chem. Soc.* **1979**, *101*, 4410–4412. (b) Huggins, J. M.; Bergman, R. G. Mechanism, regiochemistry, and stereochemistry of the insertion reaction of alkynes with methyl(2,4-pentanedionato)(triphenylphosphine)nickel. A cis insertion that leads to trans kinetic products. *J. Am. Chem. Soc.* **1981**, *103*, 3002-3011. (c) Yamamoto, A.; Suginome, M. Nickel-Catalyzed trans-Alkynylboration of Alkynes via Activation of a Boron−Chlorine Bond. *J. Am. Chem. Soc.* **2005**, *127*, 15706-15707. (d) Clark, C.; Incerti-Pradillos, C. A.; Lam, H. W. Enantioselective Nickel-Catalyzed *anti*-Carbometallative Cyclizations of Alkynyl Electrophiles Enabled by Reversible Alkenylnickel *E/Z* Isomerization. *J. Am. Chem. Soc*. **2016**, *138*, 8068-8071. (e) Shimkin, K. W.; Montgomery, J. Synthesis of Tetrasubstituted Alkenes by Tandem Metallacycle Formation/Cross-Electrophile Coupling. *J. Am. Chem. Soc.* **2018**, *140*, 7074-7078. (f) Kumar, G. R.; Kumar, R.; Rajesh, M.; Reddy, R. S. A nickel-catalyzed anti-carbometallative cyclization of alkyne–azides with organoboronic acids: synthesis of 2,3-diarylquinolines. *Chem. Commun.* **2018**, *54*, 759-762.

(33) Krasovskiy, A.; Lipshutz, B. H. Ligand Effects on Negishi Couplings of Alkenyl Halides Arkady Krasovskiy and Bruce H. Lipshutz. *Org. Lett.* **2011**, *13*, 3818-3821.

(34) This hypothesis is supported by the fact that Hartwig and Robbins observe similar diastereoselectivity under both electrophilic (protic) trapping conditions and reducing (hydridic) conditions with triethylsilane.

(35) The Ni(II) bipyridine complexes used in this study can be easily synthesized in one step by refluxing the appropriate halide salt in anhydrous ethanol. For representative procedures to synthesize these complexes, see: (a) Zheng, S.; Primer, D. N.; Molander, G. A. Nickel/Photoredox-Catalyzed Amidation via Alkylsilicates and Isocyanates. *ACS Catal.* **2017**, *7*, 7957-7961. (b) Awad, D. J.; Conrad, F.; Koch, A.; Schilde, U.; Pöppl, A.; Strauch, P. 1,10-Phenanthroline-dithiolate mixed ligand transition metal complexes. Synthesis, characterization and EPR spectroscopy. *Inorg. Chim. Acta* **2010**, *363*, 1488-1494. (c) Khrizanforov, M.; Khrizanforova, V.; Mamedov, V.; Zhukova, N.; Strekalova, S.; Grinenko, V.; Gryaznova, T.; Sinyashin, O.;

Budnikova, Y. Single-stage synthetic route to perfluoroalkylated arenes via electrocatalytic cross-coupling of organic halides using Co and Ni complexes. *J. Organomet. Chem.* **2016**, *820*, 82-88. (d) Xiao, Y.-L.; Min, Q.-Q.; Xu, C; Wang, R. W.; Zhang, X. Nickel-Catalyzed Difluoroalkylation of (Hetero)Arylborons with Unactivated 1-Bromo-1,1-difluoroalkanes. *Angew. Chem., Int. Ed.* **2016**, *55*, 5837-5841.

(36) (a) Barluenga, J.; Florentino, L.; Aznar, F.; Valdés, C. Synthesis of Polysubstituted Olefins by Pd-Catalyzed Cross-Coupling Reaction of Tosylhydrazones and Aryl Nonaflates. *Org. Lett.* **2011**, *13*, 510-513. (b) Wen, H.; Zhang, L.; Zhu, S.; Liu, G.; Huang, Z. Stereoselective Synthesis of Trisubstituted Alkenes via Cobalt-Catalyzed Double Dehydrogenative Borylations of 1-Alkenes. *ACS Catal.* **2017**, *7*, 6419-6429.

(37) Li, B.-J.; Li, Y.-Z.; Lu, X.-Y.; Liu, J.; Guan, B.-T.; Shi, Z.-J. Cross-coupling of aryl/alkenyl pivalates with organozinc reagents through nickel-catalyzed C-O bond activation under mild reaction conditions. *Angew. Chem., Int. Ed.* **2008**, *47*, 10124-10127.

(38) (a) Jana, R.; Tunge, J. A. A homogeneous, recyclable rhodium(I) catalyst for the hydroarylation of Michael acceptors. *Org. Lett.* **2009**, *11*, 971–974. (b) Jana, R.; Tunge, J. A. A Homogeneous, Recyclable Polymer Support for Rh(I)-Catalyzed C–C Bond Formation. *J. Org. Chem.* **2011**, *76*, 8376-8685.

(39) Wu, K.; Sun, N.; Hu, B.; Shen, Z.; Jin, L.; Hu, X. Geometry-Constrained Iminopyridyl Palladium-Catalyzed Hydroarylation of Alkynes to Prepare Tri-substituted Alkenes Using Alcohol as Reductant. *Adv. Synth. Catal.* **2018**, *360*, 3038-3043.

(40) (a) Song, C. E.; Jung, D.-u.; Choung, S. Y.; Roh, E. J.; Lee, S.-g. Dramatic Enhancement of Catalytic Activity in an Ionic Liquid: Highly Practical Friedel-Crafts Alkenylation of Arenes with Alkynes Catalyzed by Metal Triflates. *Angew. Chem., Int. Ed.* **2004**, *43*, 6183-6185. (b) Choi, D. S.; Kim, J. H.; Shin, U. S.; Deshmukh, R. R.; Song, C. E. Thermodynamically- and kinetically-controlled Friedel-Crafts alkenylation of arenes with alkynes using an acidic fluoroantimonate(v) ionic liquid as catalyst. *Chem Commun.* **2007**, 3482-3484. (c) Jones, R. C.; Gałęzowski, M.; O'Shea, D. F. Synthesis of Trisubstituted Alkenes via Direct Oxidative Arene–Alkene Coupling. *J. Org. Chem.* **2013**, *78*, 8044-8053.

(41) (a) Córsico, E. F; Rossi, R. A. Sequential Reactions of Trimethylstannyl Anions with Vinyl Chlorides and Dichlorides by the $S_{RN}1$ Mechanism Followed by Palladium-Catalyzed Cross-Coupling Processes. *J. Org. Chem.* **2004**, *69*, 6427-6432. (b) Terao, Y.; Nomoto, M.; Satoh, T.; Miura, M.; Nomura, M. Palladium-Catalyzed Dehydroarylation of Triarylmethanols and Their Coupling with Unsaturated Compounds Accompanied by C−C Bond Cleavage. *J. Org. Chem.* **2004**, *69*, 6942-6944.

(42) Huang, L.; Biafora, A.; Zhang, G.; Bragoni, V.; Gooßen, L. J. Regioselective C-H Hydroarylation of Internal Alkynes with Arenecarboxylates: Carboxylates as Deciduous Directing Groups. *Angew. Chem., Int. Ed.* **2016**, *55*, 6933-6937.

(43) Masai, H.; Matsuda, W.; Fujihara, T.; Tsuji, Y.; Terao, J. Regio- and Stereoselective Synthesis of Triarylalkene-Capped Rotaxanes via Palladium-Catalyzed Tandem Sonogashira/Hydroaryl Reaction of Terminal Alkynes. *J. Org. Chem.* **2017**, *82*, 5449-5455.