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Bench-Stable Nickel Precatalysts with Heck-type Activation
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Supporting Information

ABSTRACT: Herein, we report the synthesis and characterization of a new class of air- and moisture-stable phosphine-containing nickel(II) precatalysts, which activate through a Heck-type mechanism. The activities of the precatalysts are demonstrated with a carbonyl−ene coupling reaction.

INTRODUCTION

Nickel catalysis is important for providing access to structural motifs found in natural products and therapeutics.1 Nickel offers unique properties relative to other more expensive transition metals, such as the accessibility of multiple oxidation states,2 and may demonstrate reactivity complementary to that of palladium in a variety of coupling reactions.3 Despite the utility of nickel as a catalyst, the limited number of sources of this transition metal in its lower oxidation states, such as Ni(0), has inhibited the development and broader adoption of new synthetic methods. Many Ni(0) complexes, such as Ni(COD)2 (COD = 1,5-cyclooctadiene), are unstable in the presence of even moderate amounts of oxygen, light, heat, and water, thereby necessitating Schlenk line techniques and/or glovebox usage.4 In comparison, Ni(II) species, such as NiCl2, tend to display greater stability under common ambient conditions and often are comparatively less expensive. However, reduction to an active catalyst, for example a Ni(0) species, often requires reagents or conditions to which many common functional groups would not be compatible.5

In order to address these challenges and limitations,6 multiple research groups4,5,7−12 have sought to develop air- and water-stable Ni(II) complexes that have both the desired stability of Ni(II) and provide an active catalyst in situ under mild conditions (Figure 1a). Many such “precatalysts” are effective for a number of transformations, including C−C and C−N bond-forming reactions. Common modes of activation to Ni(0) include the use of high temperatures and Grignard reagents. An exception is (PPh3)2Ni(ortho-tolyl)Cl (Ni-1),4 which we demonstrated can be activated at room temperature with a silyl triflate to yield a proposed cationic nickel species (Figure 1b). Transmetalation between two nickel complexes followed by reductive elimination of a nickel biaryl species then provides the active Ni(0). Although this process occurs under relatively mild conditions, only a maximum of 50% of the Ni-1 precatalyst is transformed into active Ni(0) species.4

Ni(COD)2. As shown in Figure 1c, the Ni(II) precatalysts were designed to include an aryl ligand with an appended alkene chain. Activation with a triflate source, we reason, creates a cationic nickel species that undergoes alkene coordination, migratory insertion, and β-hydride elimination to afford the desired Ni(0) species. Thus, unlike Ni-1 or the precatalysts described by other groups, activation would occur under relatively mild conditions and avoid wasting 50% of the nickel precatalyst.

RESULTS AND DISCUSSION

As shown in Figure 2, seven Ni-complexes, each stable for a period of at least 6 months in their solid state, were synthesized by transmetalation (Method A) or oxidative addition (Method B) methods. The precatalysts were designed to bear unique...
combinations of aromatic, appended alkene, and phosphine ligands. In Method A, the corresponding Grignard reagent prepared from aryl halide 2–6 was added dropwise to (PR₃)₂NiCl₂ or (PR₃)₂NiBr₂ in THF to generate Ni-2–Ni-6 respectively.¹⁴ Notably, when using Grignard and Ni(II) substrates with mismatched halide ligands, a mixture of bromo- and chloro-precatatalyst was obtained. This was easily remedied by treating the mixture with a solution of excess LiCl to isolate the pure chloride-containing precatatalyst. In synthesis Method B, the corresponding aryl substrate was treated with Ni(COD)₂ and PPh₃ in THF. While this method provided a moderate improvement in the yield of Ni-6, it led to degradation in the case of substrates Ni-3a and Ni-3b and lower yields of Ni-2.

Crystals suitable for X-ray crystallography were obtained for Ni-2, Ni-3a, Ni-3b, Ni-5a, and Ni-6. Each precatatalyst was revealed to have a square planar geometry for each with trans phosphine ligands, which is consistent with the singlet observed in the ³¹P NMR spectra (Table 1). Ni–P bond lengths ranged from 2.198 to 2.219 Å, which are comparable to similar complexes.¹⁶ While the aliphatic side chain was disordered in the X-ray crystal structure of Ni-2, the ¹H NMR spectrum revealed alkene isomerization and a 0.6:1 mixture of cis to trans olefins regardless of the synthetic method. Alkene isomerization to the cis olefin was also observed in the ¹H NMR spectra of Ni-3a, Ni-3b, and Ni-4 and further confirmed by X-ray crystallography in the case of the first two.

With the Ni-2–Ni-6 precatalysts in hand, we initially explored their catalytic activity in a carbonyl–ene reaction between benzaldehyde (7) and 1-octene (8) at room temperature (Table 2). Precatalyst activation at 20 mol % loadings was achieved using TESOTf (1.75 equiv) and Et₃N (6 equiv). As shown in Table 2, entry 3, the use of Ni-2 resulted in the formation of the desired linear product 9 in 93 and 95% yield after 24 and 48 h, respectively. Gratifyingly, Ni-2 not only was successfully activated under these conditions but also displayed catalytic activity comparable to that of the widely used Ni(COD)₂/PPh₃ (Table 2, entry 1). Interestingly, when 1 equiv of COD was added to the reaction with Ni-2, the yield of 9 dropped to 86% in 48 h (data not shown). In contrast, Ni-3a (Table 2, entry 4), which is sparingly soluble in toluene, yielded only trace product after 48 h. The use of precatalysts Ni-3b (Table 2, entry 5), Ni-4 (Table 2, entry 6), or Ni-5a (Table 2, entry 7) also resulted in poor to moderate yields of 9. Precatalyst Ni-5b featuring the PCy₂Ph ligand¹⁵ provided a mixture of the linear (9) and branched (10) products in 13 and 47% yield, respectively. This is noteworthy given the comparable performance of Ni(COD)₂/PCy₂Ph (Table 2, entry 9), which undergoes a more conventional activation pathway to generate the same active catalyst. Finally, Ni-6, which differs from Ni-2 by the presence of a trisubstituted alkene, also provided 9 in a favorable yield of 84%, albeit requiring a more prolonged 48 h reaction time.

Having observed promising reactivity between aldehyde 7 and alkene 8 in the presence of 20 mol % Ni-2 and Ni-6, the same carbonyl–ene transformation was repeated at reduced precatalyst loadings of 5 mol % for a reaction time of 24 h. As shown in Table 3, the yield of product 9 was highest for Ni-2 (entry 4). This improved yield with Ni-2 relative to Ni(COD)₂/PPh₃ is consistently observed with multiple substrates (Table 4). Decreasing the catalyst loading of Ni-6, which was shown above to perform more sluggishly than Ni-2, greatly reduced the product yield (ca. 37%) (Table 3, entry 5). However, heating the reaction to 60 °C aided in improving the yield of 9 to 77% (Table 3, entry 5).¹⁷

We next set out to substantiate our proposed Heck-type mechanism as the mode of precatalyst activation. We additionally wanted to explore the potential for thermal activation, as heating improved the yield of 9 with Ni-6. Indeed, Heck activation product 11 was observed by HRMS and GC/MS following activation of precatalyst Ni-6 via a triflate source as well as under thermal conditions (60 °C) in the absence of triflate (Scheme 1).¹⁸,¹⁹ The ability of this complex to activate under multiple conditions bodes well for greater substrate functional group compatibility. Precatalyst activation under thermal conditions may broaden the scope of reactions to which these precatalysts can be applied.

**CONCLUSIONS**

Seven precatalysts featuring alkene-functionalized aryl ligands were synthesized and characterized. These bench-stable complexes activate via an intramolecular Heck-type mechanism under relatively mild conditions, specifically TESOTf or mild...
heating. Among the precatalysts developed, Ni-2 was found to outperform Ni(COD)$_2$/PPh$_3$ and Ni-1 in a carbonyl–ene reaction at different precatalyst loadings. With the potential for multiple activation conditions, we are exploring other applications of these precatalysts, especially in reactions that do not require the use of a triflate source or transmetallating reagent.

### EXPERIMENTAL SECTION

#### Materials, Methods, and General Considerations

Reactions were carried out under N$_2$ using standard glovebox and Schlenk
Table 4. Comparison of Ni-2 Activity with Ni(COD)2/PPh3 at 5 and 20 mol % Catalyst Loadings in a Carbonyl–Ene Reaction with Electron- and Electron-Rich Aldehyde Coupling Partners

| Entry | Ar-CHO | Time (h) | Catalyst loading (mol%) | %Yield of 12 using Ni-2 | %Yield of 12 using Ni(COD)2/PPh3 |
|-------|--------|---------|-------------------------|------------------------|----------------------------------|
| 1     | 1      | 18      | 5                       | 98                     | 60                               |
| 2     | 1      | 18      | 20                      | 96                     | 85                               |
| 3     | 1      | 24      | 5                       | 97                     | 66                               |
| 4     | 1      | 24      | 20                      | 95                     | 88                               |
| 5     | 1      | 18      | 5                       | 22                     | 9                                |
| 6     | 1      | 18      | 20                      | 47                     | 36                               |

“Yields determined by 1H NMR with MeNO2 added after quenching as an internal standard for NMR quantification. Reactions ran in duplicate, yields are ±2%.

Scheme 1. Evidence for Heck-type Activation of Ni-6 Both Thermally and via Addition of TESOTf

Techniques at ambient temperature (23–27 °C) under Ar unless otherwise noted. Diethyl ether (Et2O), tetrahydrofuran (THF), dimethylformamide (DMF), and dichloromethane (DCM) were degassed by sparging with nitrogen and dried via passage through a column of activated alumina on a Glass Contour solvent purification system. Methanol (>99.8%) and pentane were used as received. Complexes (PPh3)2NiBr2, (PPh3)2NiCl2, and (PPh3)2Ni(o-toly)Cl were prepared according to previously published procedures. Authentic samples of compounds 9 and 10 were synthesized via previously published methods. Purity was determined by 31P, 1H, and 13C NMR. NMR chemical shifts are reported in ppm relative to TMS (13C, 1H) and 85% H3PO4 (31P, as an external standard). Unless otherwise noted, NMR spectra were collected at room temperature (23–27 °C). Gas chromatography (GC) analyses were performed on an Agilent 7890A GC system with an autosampler and a 5% (phenyl)-methylpolysiloxane column coupled to a quadrupole MSD. Dodecane (1 equiv) was used as an internal standard for determination of yields relative calibration curves to determine yield. Melting points were collected on an electrothermal apparatus using glass capillaries. infrared spectroscopy (IR) spectra were collected using an Agilent Cary 630 FT-IR spectrometer equipped with an ATR accessory. Peaks from the fingerprint region were omitted from the report for clarity. High-resolution mass spectroscopy (HRMS) analysis was performed on a Bruker Daltonics APEXIV 4.7 T FT-ICR-MS outfitted with either an electrospray ionization (ESI) or an IonSense DART ion source. X-ray diffraction was performed on a Bruker APEX. Elemental analyses (EA) were performed by Atlantic Microlabs, Inc., on the complexes that did not successfully crystallize.

General Procedures for Synthesis of Nickel Complexes. Bromide Grignard Synthesis. In a glovebox, solid magnesium (1.1 equiv) was added to a solution of arene (1 equiv) in THF (0.5 M) in a 2 dram vial. The vial was sealed tightly and removed from the box. This reaction was stirred for 24 h at room temperature and used without any purification. Additionally, a color change from clear to brown was observed during these reactions.

Chloride Grignard Synthesis. In a glovebox, solid magnesium (1.1 equiv) was added to a solution of arene (1 equiv), iodine (0.01 equiv) in THF (0.5 M) in a Schlenk flask. The flask was then sealed, removed form the glovebox, and heated to 60 °C. The reaction was stirred for 24 h and then cooled to room temperature. The Grignard was used without further purification.

Transmetalation Method (Method A). Under Ar gas, nickel complex (PR3)2NiX2 was dissolved in THF (0.15 M) in an oven-dried round-bottomed flask containing a magnetic stir bar. The solution was cooled to 0 °C with an ice bath, and then the Grignard reagent (1 equiv) was added dropwise via syringe. The solution was stirred for 5 min, after which the reaction was quenched with 2 mL of MeOH. The solution was then evaporated to dryness under reduced pressure to a sticky tar. MeOH (5 mL) was added and the mixture was sonicated until a yellow solid precipitated (ca. 2 min). The precipitate was collected by vacuum filtration, washed (with MeOH, 2 × 25 mL, and pentane, 1 × 10 mL) and dried under high vacuum to yield the complex. The complexes were then purified via recrystallization from DCM/MeOH with a stream of Ar gas used to evaporate the DCM.

Oxidative Addition Method (Method B). In a glovebox, Ni(COD)2 (1 equiv) and PPh3 (2 equiv) were dissolved in THF (0.4 M). The desired arene (1.1 equiv) was added and the vial was sealed, removed from the glovebox, and stirred for 18 h at room temperature. The solution was then opened to air and filtered through a plug of Celite. The solution was then evaporated to dryness under reduced pressure to a sticky tar. MeOH (5 mL) was added, and the mixture was sonicated until a yellow solid precipitated (~2 min). The precipitate was collected by vacuum filtration, rinsed with MeOH (2 × 25 mL), and pentane (10 mL), and dried under high vacuum to yield the complex. The complexes were purified via recrystallization from DCM/MeOH with evaporation under a stream of argon.
Synthesis and Characterization of Complexes. **Ni-2.** The Grignard of 2 (6 mL, 3 mmol, 0.5 M) was prepared via reaction of 500 mg of 2 and 80 mg of powdered magnesium in 6 mL of THF, using the general procedure for preparation of chloride Grignard. Then, **Ni-2** was prepared via dropwise addition of 6 mL of this Grignard solution to 1.96 g of (PPh$_3$)$_2$NiCl in 20 mL of THF following the general transmetalation procedure (Method A). Yield: 790 mg (35%). Alternatively, **Ni-2** was prepared via the general oxidative addition method (Method B) by addition of 1.47 g of 2 to 2.20 g of Ni(COD)$_2$ and 4.20 g of PPh$_3$ in 20 mL of THF. Yield: 1.68 mg (28%). Crystals suitable for single-crystal X-ray diffraction were grown by the slow diffusion of methanol into a saturated solution of **Ni-2** in dichloromethane at −30 °C. **31P NMR (400 MHz, C$_6$D$_6$, 223 K, δ):** 7.72 (bs, 1H), 7.47 (d, δ = 7.7 Hz, 1H), 7.39 (d, δ = 7.7 Hz, 1H), 7.29−7.36 (m, 1H), 7.15 (s, 4H), 6.63 (t, δ = 8.0 Hz, 2H), 6.24−6.38 (m, 3H), 5.55 (q, δ = 8.0 Hz, 1H), 5.27 (m, 1H), 4.59 (m, 2H), 3.83 (d, δ = 9.0 Hz, 1H), 3.77 (d, δ = 9.0 Hz, 1H), 1.59 (d, δ = 6.7 Hz, 1H), 1.36 (d, δ = 6.7 Hz, 3H) ppm. **13C NMR (101 MHz, CD$_2$Cl$_2$, 258 K, δ):** 143.8 (t, $\delta_{13C}$ = 5.4 Hz), 110.0, 37.4, 12.8, 1.5, 0.1 ppm. **31P NMR (121 MHz, C$_6$D$_6$, δ$_0$):** 21.1 ppm. IR (powder ATR, cm$^{-1}$): 3050.9. **HRMS-ESI (m/z):** Predicted: [C$_{46}$H$_{41}$NiP$_2$]+: 729.1968 m/z. Found: [C$_{46}$H$_{41}$NiP$_2$]+: 729.1968 m/z. Anal. Calc. for C$_{46}$H$_{41}$NiP$_2$: C, 73.67; H, 5.51. Found: C, 73.49; H, 5.39. Melting Point: 132−133 °C.

**Ni-3a.** The Grignard of 3 (12 mL, 6 mmol, 0.5 M) was prepared via reaction of 1.58 g of 3 and 160 mg of powdered magnesium in 12 mL of THF, using the general procedure for preparation of bromide Grignard. Then, **Ni-3a** was prepared via dropwise addition of 12 mL of this Grignard solution to 3.92 g of (PPh$_2$Me)$_2$NiCl in 40 mL of THF following the general transmetalation procedure (Method A). Yield: 1.51 g (32%). The general procedure was followed except the precatalyst underwent a halogen exchange via stirring with LiCl sat. THF for 18 h. To isolate, the mixture was filtered through a plug of Celite, concentrated, and sonicated in 5 mL MeOH to give a yellow solid, which was washed 3 × 25 mL with MeOH. This was done in order to remove any of the bromide-containing complex. Crystals suitable for single-crystal X-ray diffraction were grown by the slow diffusion of pentane into a dichloromethane solution of **Ni-3a** at −30 °C.

**Ni-3b.** The Grignard of 3 (3 mL, 1.5 mmol, 0.5 M) was prepared via reaction of 395 mg of 3 and 40 mg of powdered magnesium in 3 mL of THF, using the general procedure for preparation of bromide Grignard. Then, **Ni-3b** was prepared via dropwise addition of 3 mL of this Grignard solution to 981 mg of (PPh$_2$Me)$_2$NiCl in 10 mL of THF following the general transmetalation procedure (Method A). Yield: 280 mg (28%). The general procedure was followed except the precatalyst underwent a halogen exchange via stirring with LiCl saturated THF for 18 h. To isolate, the mixture was filtered through a plug of Celite, concentrated, and sonicated in MeOH to give a yellow solid, which was washed 3 × 25 mL with MeOH. This was done in order to remove any of the bromide-containing complex. Crystals suitable for single-crystal X-ray diffraction were grown by the slow diffusion of pentane into a toluene solution of **Ni-3b** at −30 °C.

**Ni-4.** The Grignard of 4 (8 mL, 4 mmol, 0.5 M) was prepared via reaction of 1.08 g of 4 and 53 mg of powdered magnesium in 8 mL of THF, using the general procedure for preparation of bromide Grignard. Then, **Ni-4** was prepared via dropwise addition of 8 mL of this Grignard solution to 1.77 g of (PPh$_2$Me)$_2$NiCl in 30 mL of THF following the general transmetalation procedure (Method A). Yield: 1.75 g (52%). **31P NMR (400 MHz, C$_6$D$_6$, δ$_0$):** 7.88 (s, 1H), 7.50 (s, 1H), 7.33−7.45 (m, 1H), 7.01 (s, 1H), 6.80 (d, δ = 8.4 Hz, 1H), 5.71 (d, δ = 8.4 Hz, 1H), 5.41 (d, δ = 7.0 Hz, 1H), 4.61 (t, δ = 7.0 Hz, 2H), 2.01 (d, δ = 7.0 Hz, 3H), 1.21 (s, 1H), 1.05 (s, 8H) ppm. **13C NMR (101 MHz, CCl$_2$D$_2$, δ):** 143.9, 142.6, 135.2 (t, $\delta_{13C}$ = 5.5 Hz), 136.3, 132.9 (t, $\delta_{13C}$ = 21.8 Hz), 130.0, 128.0 (t, $\delta_{13C}$ = 4.8 Hz), 120.6, 113.2, 103.6, 34.0, 31.6, 10.2 ppm. **31P NMR (121 MHz, C$_6$D$_6$, δ$_0$):** 22.8 ppm. Anal. Calc. for C$_{42}$H$_{36}$BeNiOP$_2$: C, 69.04; H, 5.56. Found: C, 68.77; H, 5.70. HRMS-ESI (m/z): Predicted: [C$_{42}$H$_{36}$BeNiOP$_2$]+: 771.2459 m/z. Found: [C$_{42}$H$_{36}$BeNiOP$_2$]+: 771.2459 m/z. IR alkene stretch (ATR, cm$^{-1}$): 3052.9. Melting point: 167−168 °C.

**Ni-5a.** The Grignard of 5 (3 mL, 1.5 mmol, 0.5 M) was prepared via reaction of 437 mg of 5 and 40 mg of powdered magnesium in 3 mL of THF, using the general procedure for preparation of bromide Grignard. Then, **Ni-5a** was prepared via dropwise addition of 3 mL of this Grignard solution to 981 mg of (PPh$_2$Me)$_2$NiCl in 10 mL of THF following the general transmetalation procedure (Method A). Yield: 735 mg (59%). The general procedure was followed except the pre-catalyst underwent halogen exchange reaction via stirring in MeOH and toluene (8:1, 0.1 M) with 5 equiv of LiCl for 18 h. To isolate, the reaction was concentrated and sonicated in MeOH to give a yellow solid, which was washed 3 × 25 mL with MeOH. This was done in order to remove any of the bromide-containing complex. Crystals suitable for single-crystal X-ray diffraction were grown by the slow diffusion of pentane into a toluene solution of **Ni-5a** at −30 °C.

**Ni-5b.** The Grignard of 5 (20 mL, 10 mmol, 0.5 M) was prepared via reaction of 2.91 g of 5 and 266 mg of powdered magnesium in 20 mL of THF, using the general procedure for preparation of bromide Grignard. Then, **Ni-5b** was prepared via dropwise addition of 20 mL of this Grignard solution to 6.78 g of (PC$_2$Ph)$_2$NiCl in 60 mL of THF following the general transmetalation procedure (Method A). Yield: 5.81 g (68%). The general procedure was followed except the pre-catalyst underwent halogen exchange reaction via stirring in MeOH and toluene (8:1, 0.1 M) with 5 equiv of LiCl for 18 h. To isolate, the reaction was concentrated and sonicated in MeOH to give a yellow solid, which was washed 3 × 25 mL with MeOH. This was done in order to remove any of the bromide-containing complex. Crystals suitable for single-crystal X-ray diffraction were grown by the slow diffusion of pentane into a toluene solution of **Ni-5b** at −30 °C.
[C₆H₅NiOP₂]⁺: 817.4155 m/z. IR alkene stretch (ATR, cm⁻¹): 3043.0. Melting point: 138 °C.

Ni-6. The Grignard of 6 (2 mL, 1 mmol, 0.5 M) was prepared via reaction of 180 mg of 6 and 20 mg of powdered magnesium in 2 mL of THF, using the general procedure for preparation of chloro Grignard. Then, Ni-6 was prepared via dropwise addition of 2 mL of this Grignard solution to 654 mg of (PPh₃)₂NiCl in 5 mL of THF following the general transmetalation procedure (Method A). Yield: 305 mg (40%). Alternatively, Ni-6 was prepared via the general oxidative addition method (Method B) by addition of 198 mg of 275 mg of Ni(COD)₂ and 524 mg of PPh₃ in 10 mL of THF. Yield: 410 mg (53%). Crystals suitable for single-crystal X-ray diffraction were grown by the slow diffusion of methanol into a dichloromethane solution of Ni-6 at −30 °C. ¹H NMR (400 MHz, CD₂Cl₂, δ): 7.74 (s, 11H), 7.73 (d, J = 7.4 Hz, 2H), 7.01 (s, 18H), 6.59 (brs, 1H), 6.28–6.41 (m, 1H), 4.56 (s, 1H), 4.00 (d, J = 7.4 Hz, 2H), 1.62 (s, 3H), 1.47 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃, 125 K, δ): 147.2, 136.5, 135.2 (t, 1JCP = 5.8 Hz, 1H), 132.3, 123.2 (t, 1JCP = 21.5 Hz, 1H), 130.2, 128.3 (t, 1JCP = 5.0 Hz), 123.6, 123.4, 122.7, 68.3, 39.3, 25.8, 17.9 ppm. ¹⁹F NMR (121 MHz, CDCl₃, δ): 21.1 ppm. HRMS-ESI (m/z): Predicted: [C₅₁H₆₉NiOP₂]⁺: 727.2188. Found: [C₅₁H₆₉NiOP₂]⁺: 727.2168. Anal. Calcd for 85% Ni-6: C 72.74; H 5.61. Found: C, 72.52; H, 5.53. IR alkene stretch (ATR, cm⁻¹): 3039.9. Melting point: 154 °C.

Procedure and Characterization for the Carbonyl–Ene Reaction. In a glovebox, the desired precatalyst (5–20 mol %) was added to a 2 dram vial containing a solution of alken 1 (1 mmol, 5 equiv), triethylamine (1.2 mmol, 6 equiv), and aldehyde (0.20 mmol, 1 equiv) dissolved in toluene (2 mL). While 1-ocetene and benzaldehyde were used, dodecane (0.2 mmol, 1 equiv) was also added as internal standard for the subsequent GC analysis. This mixture was stirred for 30 s after which TESOTf (1.75 equiv, 0.35 mmol) was added as internal standard for the subsequent GC analysis. This reaction mixture through a plug of silica, which was then washed 2 mL of dichloromethane. The filtrate was then concentrated to dryness, dissolved in CDCl₃, and 1 equiv of nitromethane added as an internal standard for ¹H NMR analysis.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00351.

General experimental procedures, synthesis of aryl precursors, spectral data, and X-ray crystallographic data (PDF)

Accession Codes
CCDC 1583496–1583500 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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(14) The chloride of 5 was also synthesized and used to form the corresponding Ni-complex, but the yield was lower than when starting from bromide 5. See SI for more information.

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(18) Biaryl formation was not observed under thermal or TESOTf activation conditions with Ni-2 – Ni-6.

(19) Ni-6 was chosen for activation tests due to the Heck product’s inability to isomerize. Additionally, 11 was identified based on comparison of the retention time and fragmentation pattern of an authentic sample.

(20) Due to the instability of Ni-2 in solution, a full carbon spectra was unattainable. In order to confirm purity for this complex, elemental analysis was obtained.