ORGANOMETALLICS

Suzuki-Miyaura Csp²-Csp² Cross-Couplings Employing Nickel(II) **Pincer Precatalysts: Mechanistic Investigations**

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Cite This: https://doi.org/10.1021/acs.organomet.1c00033 **Read Online** ACCESS Metrics & More Article Recommendations **SUPPORTING Information** ABSTRACT: This study investigates the mechanism of Suzuki-Br Miyaura Csp²-Csp² cross-couplings facilitated by PCP-type nickel(II) Ph pincer complexes. By employing a combination of standard experimental p-tol and theoretical methods, it is proposed that a nickel(I)/(III) cycle is

INTRODUCTION

this transformation.

The Suzuki–Miyaura (SM) reaction is a particularly powerful, efficient, and reliable tool for forming carbon-carbon bonds that has found an array of applications across organic and materials synthesis.¹ However, with the exception of crosscouplings featuring Csp³ electrophiles and/or Csp³ nucleophiles,² the majority of SM transformations arguably continue to rely on palladium catalysis rather than cheaper, more earth abundant alternatives such as nickel.³ The subtleties of the mechanisms of nickel-catalyzed SM Csp²-Csp² couplings are not as well understood as the analogous palladium-catalyzed processes.^{3b,4,5} This may be due to factors including the greater propensity for fundamental nickel intermediates to speciate under the reaction conditions, the increased viability of both heterolytic and homolytic activation pathways involving nickel, and the inherent paramagnetism of many nickel species that can complicate reaction monitoring by NMR spectroscopy.^{4b,6} To improve the efficiency and extend the scope of reactions within this manifold, detailed investigations of the mechanisms of nickel-catalyzed SM Csp²-Csp² couplings are still required.

involved in this reaction and single-electron pathways likely operate in

Nickel pincers are a readily accessible class of complexes that have found various applications in catalysis.⁷ In addition to their ease of preparation, PCP-type nickel pincers such as molecules 1 and 2 are air- and moisture-stable (Figure 1).^{8,9} This class of complexes typically also features high thermal stability,¹⁰ which is important in enabling more tractable



Figure 1. Examples of PCP-type nickel(II) pincer complexes.

mechanistic studies to be undertaken in nickel-catalyzed reactions.^{8b} Although it has been demonstrated that nickel(II) pincers can promote SM cross-couplings,¹¹ relatively few studies have explored the underlying mechanisms that underpin these processes in detail.^{5h} Consistent with investigations of SM reactions employing other families of well-defined nickel catalysts,5 the nature of precatalyst activation and the implication/competence of catalytically active nickel(I) species are important factors to consider and explore.^{3b,4,5} To this end, we sought to investigate the capacity for PCP-type nickel pincers to promote SM cross-couplings and better understand how such species may facilitate these reactions employing a combination of experimental and theoretical methods.

Ph

p-tol

[Ph(PCP)Nill(p-tol)]

chemically competent

RESULTS AND DISCUSSION

B(OH)

[^{Ph}(PCP)Ni^{ll}(R)] single-electron

pathway

In preliminary experiments, we demonstrated for the first time that nickel complexes 1 and 2 can facilitate SM reactions (Table 1, entries 1-3). While precatalyst 1 was superior to 2, each of these processes delivered biaryl 5 in moderate yields with incomplete conversion. Minimal nucleophile homocoupling was observed under these conditions {<5% yield of biphenyl (6); see Supporting Information }. Unsurprisingly, performing the reaction at 80 °C afforded an even lower yield and poorer conversion (entry 4). Little or no cross-coupling occurred in the presence of either water or air and in the absence of either catalyst or base (entries 5-8). While product

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 Table 1. Nickel-Catalyzed Suzuki–Miyaura Reactions:

 Preliminary Experiments^a

| p-tol—Br 3a | (HO) ₂ B−Ph 4a (1.2 equiv) ^{10%} Ni 1 ² equiv K ₃ PO ₄ .H ₂ O PhMe, reflux, Ar | P-tol—Ph 5 |
|----------------|--|------------------------|
| entry | variation | yield (%) ^b |
| 1 | none | 55 (65) |
| 2 | 5% Ni 1 | 49 (61) |
| 3 | 10% Ni 2 instead of Ni 1 | 41 (56) |
| 4 | 80 °C instead of reflux | 23 (35) |
| 5 | 2:1 $PhMe/H_2O$ instead of PhMe | 2 (5) |
| 6 | air instead of Ar | 0 (<1) |
| 7 | no Ni 1 | 0 (<1) |
| 8 | no K ₃ PO ₄ | 0 (<1) |
| 9 | 1.7 equiv of $PhB(OH)_2$ | 77 (87) |
| 10 | 5% Ni 1, 1.7 equiv of $PhB(OH)_2$ | 83 (89) |
| 11 | 2.2 equiv of $PhB(OH)_2$ | 88 (100) |

"Reactions performed employing 100 μ mol of 3a. ^bYield of 5 determined by gas chromatography (GC) with the aid of a calibrated internal standard (average of 2 experiments); consumption of 3a is shown in parentheses.

5 was not formed in the control experiment without $[^{Ph}(PCP)NiBr]$ (1) (Table 1, entry 7), we observed the formation of biphenyl in 9% yield (see Supporting Information).¹² This suggested that raising the nucleophile loading would be necessary for developing an enhanced SM process. Accordingly, we found that increasing the stoichiometry of phenylboronic acid was crucial to establishing an efficient reaction (Table 1, entries 9–11; Table 2, entry 1). This allowed us to identify optimal conditions that allowed for a high-yielding cross-coupling employing only 1% of precatalyst 1 (Table 2, entry 2).¹³

While we could couple aryl bromides efficiently, reactions employing 4-chlorotoluene or p-tolyl triflate proceeded at very low conversion (Table 2, entries 3 and 4). In addition,

Table 2. Nickel-Catalyzed Suzuki–Miyaura Reactions: Influence of Reaction Parameters and Scope^a

| p-tol—Br 3a | (HO) ₂ B−Ph 4a (2.2 equiv) | P-tol Ph 5 |
|----------------|--|------------------------|
| entry | variation | yield (%) ^b |
| 1 | none | 90 (100) |
| 2 | 1% Ni 1 | 95 (98) |
| 3 | p-tol-CI instead of 3a | 12 (38) |
| 4 | p-tol–OTf instead of 3a | 10 |
| 5 | PhBpin instead of 4a | 0 (<1) |
| 6 | PhBF ₃ K instead of 4a | 0 (<1) |
| 7 ^c | PhBpin instead of 4a | 0 (<1) |
| 8 ^c | PhBF ₃ K instead of 4a | 0 (<1) |
| 9 | + 1 equiv of TEMPO | <1 (2) |

"Reactions performed employing 100 μ mol of 3a. ^bYield of 5 determined by GC with the aid of a calibrated internal standard (average of 2 experiments); electrophile consumption is shown in parentheses. ^cExperiment performed using a 2:1 PhMe/H₂O solvent mixture. phenylboronic acid pinacol ester and potassium phenyltrifluoroborate were not viable coupling partners either under the standard conditions or in toluene/water solvent mixtures (entries 5–8). The poor reactivity of the aryl triflate is consistent with an SM coupling mechanism that features predominant single-electron pathways.^{5h} This was reinforced by an experiment demonstrating reaction inhibition in the presence of the radical scavenger TEMPO (entry 9). These observations, the above-mentioned influence of nucleophile loading on reaction efficiency, and the dearth of studies concerning the mechanism of SM cross-couplings mediated by nickel(II) pincers,^{Sh} when taken together, prompted us to explore the reaction mechanism further.

Nickel complex 1 is a d⁸ low-spin 16-electron species with square planar coordination geometry confirmed by X-ray crystallography.¹⁴ We employed continuous shape measurements to assess the coordination environment of the d⁸ center in complex 1.¹⁵ These calculations indicated that the nickel center approximates a square planar geometry, with little distortion from the D_{4h} symmetry noted.^{16,17} Thus, we anticipated that these properties would render this molecule diamagnetic, allowing us to readily monitor the SM reaction via NMR spectroscopy. In this way, we determined that the predominant resting states of the catalyst are [^{Ph}(PCP)Ni(Ph)] (7a) and [^{Ph}(PCP)Ni(*p*-tol)] (7b) during the early stages of the reaction (eq 1).¹⁸ In a competition experiment



between 4-bromo- and 4-chlorotoluene, the catalyst effectively differentiated between these electrophiles (eq 2). However, in the analogous competition experiment involving 4-bromo- and 4-iodotoluene, this differentiation was less pronounced (eq 3).

In order to study the precatalyst activation step, [^{Ph}(PCP)-NiBr] (1) and 4-bromotoluene were heated together and the reaction was monitored by ³¹P NMR spectroscopy (Figure 2A). No reaction occurred under these conditions, with similar results obtained in the presence of base. Next, we heated [^{Ph}(PCP)NiBr] (1) with *p*-tolylboronic acid, which also afforded no reaction (Figure 2B). However, we observed the formation of [^{Ph}(PCP)Ni(*p*-tol)] (7b) as the major product in



Figure 2. Stoichiometric reactions of $[^{Ph}(PCP)NiBr]$ (1) with (A) 4-bromotoluene and (B) *p*-tolylboronic acid.

the presence of K_3PO_4 .¹⁹ Analysis of the reaction mixture by GCMS indicated that homocoupling also occurred under these conditions. No reaction occurred when the same experiment was performed in the presence of TEMPO. Taken together, these data are consistent with the reaction of [^{Ph}(PCP)NiBr] (1) with the arylboronate via a single-electron pathway, and we anticipate that this process is responsible for the activation of precatalyst 1. These observations are generally consistent with the results of a study exploring the mechanism of an SM reaction promoted by a PNP-type nickel pincer.^{5h} Cyclic voltammetry experiments performed on [^{Ph}(PCP)NiBr] (1) revealed irreversible electrochemical behavior consistent with irreversible reduction (and oxidation) of this species across a range of scan rates (25–250 mV/s) (see Supporting Information).²⁰

In order to better understand the C–C bond-forming process, $[^{Ph}(PCP)Ni(p-tol)]$ (7b) and 4-bromobenzene were heated together (Figure 3A). Biaryl 5 was not formed in this experiment or when this reaction was performed in the presence of base. These observations suggest that oxidative addition precedes transmetalation in the catalytic cycle. Next, we heated $[^{Ph}(PCP)Ni(p-tol)]$ (7b) with phenylboronic acid, which delivered biaryl 5 in 51% yield (Figure 3B).²¹ Interestingly, we found that this stoichiometric reaction was less efficient in the presence of base. When the results of these stoichiometric experiments are taken together with the observations shown in eqs 1–3, it is unclear which fundamental step (oxidative addition or transmetalation) is turnover-limiting in these nickel-catalyzed SM couplings of aryl bromides.

We demonstrated that [^{Ph}(PCP)Ni(*p*-tol)] (7b) serves as a viable precatalyst for this reaction (Figure 3C).^{22,23} Taken together, the experiments shown in Figure 3 confirm the chemical competence of species 7b in the SM cross-coupling. We used Density Functional Theory (DFT) to model transmetalation from complex 7b via reaction with a phenylboronic-acid-derived free phenyl radical 8 and found that the transformation leading to nickel(III) adduct 9 is exergonic ($\Delta G = -14.3$ kcal/mol) (eq 4). DFT calculations indicated that reductive elimination from intermediate 9 to afford biaryl product 5 and nickel(I) species 10 is also energetically favorable ($\Delta G = -33.8$ kcal/mol) (eq 5).²⁴



Figure 3. Stoichiometric reactions of $[^{Ph}(PCP)Ni(p-tol)]$ (7b) with (A) 4-bromobenzene and (B) phenylboronic acid. (C) Demonstrating the competence of $[^{Ph}(PCP)Ni(p-tol)]$ (7b) under catalytic conditions. "Yield of **5** determined by GC with the aid of a calibrated internal standard (average of 2 experiments).

$$[^{Ph}(PCP)Ni(p-tol)] + Ph^{\bullet} \longrightarrow [^{Ph}(PCP)Ni(p-tol)(Ph)]^{\bullet} (4)$$
7b 8 9
$$\Delta G_{calc} = -14.3 \text{ kcal/mol}$$

$$[^{Ph}(PCP)Ni(p-tol)(Ph)]^{\bullet} \longrightarrow [^{Ph}(PCP)Ni]^{\bullet} + p-tol-Ph$$
9
$$10 5$$

$$\Delta G_{calc} = -33.8 \text{ kcal/mol}$$

$$\Delta G_{calc} = +6.9 \text{ kcal/mol}$$

To investigate the involvement of single-electron pathways in the transmetalation step, we examined the reaction of $[^{Ph}(PCP)Ni(p-tol)]$ (7b) with arylboronic acid radical probe 11 (Figure 4A). Because it is established that radical 12a rapidly cyclizes {rate constant (k) = 9.6 × 10⁹ s⁻¹ in DMSO},²⁵ we anticipated that this reaction might lead to the formation of cyclized products in preference to biaryl 13a.²⁶ In accordance with this, we observed dihydrobenzofurans 13b and 13c and we did not identify cross-coupled products 13a in the crude reaction mixture via GCMS.²⁷ However, when we performed this reaction employing bromobenzene and 5% [^{Ph}(PCP)NiBr] (1), we observed the formation of allyl-coupled product 14 in addition to dihydrobenzofurans 13b and 13c (Figure 4B). Allyl-coupled products 13b and 14 may derive from competing nickelmediated allylation reactions involving two molecules of substrate 11.28,29 Finally, we reacted bromide 15 with phenylboronic acid in the presence of $[^{Ph}(PCP)NiBr]$ (1) (Figure 4C). This reaction proceeded at low conversion, and analysis of the crude reaction mixture via GCMS indicated that the predominant organic molecules present were unreacted electrophile 15 and biphenyl (6) in addition to dihydrobenzofuran 13c. We did not detect possible cross-coupled product 2allyloxybiphenyl in this reaction by GCMS; however, we did isolate dihydrobenzofuran 16 in low yield.³



Figure 4. (A) Stoichiometric reaction of $[^{Ph}(PCP)Ni(p-tol)]$ (7b) with boronic acid 11. Investigation of the Ni-catalyzed SM cross-coupling employing: (B) nucleophile 11; (C) electrophile 15.

On the basis of the above-mentioned experiments, we propose that a Ni(I)/(III) cycle is operative in this cross-coupling reaction. It is feasible that the catalytically active Ni(I) species derives from the one-electron reduction of precatalyst [^{Ph}(PCP)NiBr] (1) by the arylboronic acid in the presence of base (Figure 5). We anticipate that oxidative



Figure 5. Outline of a possible catalytic cycle for nickel-catalyzed SM cross-couplings.

addition of the electrophile to the ensuing Ni(I) species possibly via a single-electron pathway delivers a Ni(III)–aryl intermediate. It is possible that the subsequent transmetalation step also proceeds by a single-electron pathway to afford a Ni(III) species from which reductive elimination regenerates a Ni(I) species that is capable of reacting with the electrophile to continue the process. We suggest that, while [^{Ph}(PCP)-Ni^{II}(aryl)] species, such as complex 7b, are chemically competent intermediates in this reaction, they do not feature on the primary catalytic cycle (Figure 5). This mechanistic proposal differs from the catalytic cycle that has been suggested for an SM reaction promoted by a PNP-type nickel pincer.^{Sh} This recently reported study also invokes a key on-cycle Ni(I) dimer. However, we did not obtain any experimental evidence suggesting the involvement of an analogous intermediate in this chemistry employing PCP-type nickel pincer catalysts.

CONCLUSIONS

We have demonstrated for the first time that PCP-type nickel pincers 1 and 2 can facilitate SM reactions. The findings from our associated mechanistic studies are consistent with a Ni(I)/(III) cycle in which single-electron pathways are operative in this transformation. Our results suggest that elevated temperatures are necessary for an efficient cross-coupling. This indicates that alternative strategies for substrate activation are probably required to develop milder, more practical SM Csp²–Csp² couplings and related processes with PCP-type nickel pincer catalysts, and this will be the subject of future work in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00033.

Additional experimental information and compound characterization data (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 2057111 contains 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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(17) Ligand field is well-known to have an impact on the electronic properties of nickel(II) complexes. Square planar low spin d^8 complexes tend to be diamagnetic, as a result of overlap between the ligand s orbital and the metal $d_{x^2-y^2}^2$. The s* is unoccupied, so that the eight d electrons pair up in the remaining d orbitals, resulting in observed diamagnetism of the complex.

(18) When we performed the experiment shown in eq 1 employing $[^{Ph}(PCP)Ni(p-tol)]$ (7b) in place of $[^{Ph}(PCP)NiBr]$ (1), we obtained the same results.

(19) In addition to the presence of $[^{Ph}(PCP)Ni(p-tol)]$ (7b) and $[^{Ph}(PCP)NiBr]$ (1) in this experiment, we observed the presence of a minor signal (δ_P 33.3 ppm) that we were not able to assign to a complex.

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(21) Cyclic voltammetry experiments performed on [^{Ph}(PCP)Ni(p-tol)] (7b) revealed irreversible electrochemical behavior consistent with irreversible reduction (and oxidation) of this species across a range of scan rates (25–250 mV/s) (see Supporting Information).

(22) This reaction proceeded with complete conversion of 4bromotoluene, and biphenyl was formed in 6% yield.

(23) When we performed the experiment shown in Figure 3C in the absence of base, cross-coupled product 5 was only formed in trace amounts.

(24) The geometry of $[^{Ph}(PCP)Ni(p-tol)(Ph)]^{\bullet}$ is distorted squarepyramidal where axial P–Ni–P and C_{ax} –Ni– C_{eq} angles are 142.0° and 108.7°, respectively. These angles are decreased to 136.7° and 65.3°, respectively, in the transition state for *p*-tol…Ph coupling (see Supporting Information).

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(27) When we performed the experiment shown in Figure 4A in the presence of the K_3PO_4 ·H₂O, similar results were observed and dihydrobenzofurans 13b and 13c were the major products formed. Compound 13c is volatile, and we were not able to isolate this molecule. However, we could identify this species via GCMS analysis of the reaction mixture and comparison to an authentic sample.

(28) See, for example: (a) Wang, G.; Gan, Y.; Liu, Y. Nickel-Catalyzed Direct Coupling of Allylic Alcohols with Organoboron Reagents. *Chin. J. Chem.* **2018**, *36*, 916–920. (b) Nazari, S. H.; Bourdeau, J. E.; Talley, M. R.; Valdivia-Berroeta, G. A.; Smith, S. J.; Michaelis, D. J. Nickel-Catalyzed Suzuki Cross Couplings with Unprotected Allylic Alcohols Enabled by Bidentate N-Heterocyclic Carbene (NHC)/ Phosphine Ligands. *ACS Catal.* **2018**, *8*, 86–89.

(29) The existence of this competing nickel-mediated allylation reaction from substrate 11 represents a limitation of this system as a radical probe for this nickel-catalyzed SM cross-coupling (in addition to the issue discussed in ref 30).

(30) The formation of dihydrobenzofuran **16** does not provide conclusive evidence for a radical pathway. For example, the possibility that product **16** results from the concerted oxidative addition of bromide **11** to a nickel species, followed by β -migratory insertion, transmetalation, and reductive elimination, cannot be excluded.