



Efficient Nickel Precatalysts for Suzuki-Miyaura Cross-Coupling of Aryl Chlorides and Arylboronic Acids Under Mild Conditions

Morgan E. John, Michael J. Nutt, Josephine E. Offer, Jeremy A. Duczynski, Ken Yamazaki, Tomoya Miura, Stephen A. Moggach, George A. Koutsantonis,* Reto Dorta,* and Scott G. Stewart*

Abstract: The synthesis and catalytic properties of Ni(II) complexes with the general formula Ni(NHC)[P(OR)₃](Ar)Cl are described. These complexes are air-stable and extremely effective precatalysts in the Suzuki-Miyaura cross-coupling reaction. The reaction protocols described allow for the cross-coupling of aryl chlorides and arylboronic acids, employing low catalytic loading, to deliver a large variety of functionalized biaryl compounds. For the coupling of aryl chlorides with *N*-heterocyclic boronic acids, TBAF was used as an additive to afford nitrogen-containing biaryl products. Overall, these reaction protocols operate at room or mild temperatures and can be applied to a variety of electronically and sterically differentiated coupling partners. Fundamental insights into the mechanism of this reaction, including the proposed formation of the catalytically active Ni(NHC)[P(Oi-Pr)₃] and resting state species, are also reported.

Introduction

The Suzuki-Miyaura coupling (SMC) is an invaluable approach to form carbon–carbon bonds between complex organic fragments.^[1,2] The activity, selectivity, and maturity of palladium (Pd) catalysts, achieved through decades of

ancillary ligand and precatalyst architecture development, have made them the default choice for SMCs in academic and industrial settings. However, due to the cost and low abundance of palladium, there has been an increased focus on developing nickel (Ni) catalysts as inexpensive alternatives. Nonetheless, Ni-catalysts are still less reliable and robust than their Pd counterparts^[3–5]; to achieve similar yields and selectivity across a scope of chemically simple substrates, Ni-catalysts generally require high temperatures,^[6,7] and relatively large catalytic loadings, employ expensive organometallic additives and longer reaction times, and are also generally intolerant of Lewis-basic *N*-heterocyclic coupling partners plus only a narrow range of ancillary ligands are effective (Figure 1a).^[8,9] The paucity of general, accessible, and modular Ni-precatalyst architectures further inhibits the development of Ni-catalyzed SMC reactions.

Nickel precatalysts that have been successful in thermal cross-coupling reactions, and especially in the SMC, can be separated broadly into two categories: those that are pre-ligated with an ancillary ligand (well-defined), or those that form a complex in situ with exogenous ligand (general) (Figure 1b). Ni(cod)₂ is the most popular general precatalyst for Ni SMC, but is challenging to synthesize and notoriously sensitive to air.^[10–13] As such, air-stable alternatives, Ni(cod)(DQ)^[14,15] and Ni(stb)₃^[16,17] have been developed. Well-defined Ni(0) complexes (NHC)Ni-bis(acrylate/fumarate)^[18] and Ni–phosphine/phosphite,^[19–22] so far underexplored in Ni-SMC, are also suitable precatalysts for cross-coupling. Well-defined Ni(II) complexes, in the form of [L_nNi(Ar)X], provide an alternate group of air-stable precatalysts that form coordinatively unsaturated, catalytically active Ni(0)L₂ species through an initial endogenous reduction event (Figure 1b).^[23–35]

Ni(II) precatalysts containing NHC ligands have rarely been effective for the SMC (Figure 1a, right)^[36–52] and have mostly been developed and studied for C–N coupling reactions. The weaker performance of Ni-NHC systems in the SMC is potentially because, as reported by Doyle and Sigman,^[53,54] successful ancillary ligands for Ni-catalyzed SMC must facilitate the kinetic formation of L₁Ni(II) but thermodynamically prefer a L₂Ni(II) resting state, while most Ni-NHC complexes are typically designed to exclusively form a L₁Ni species.

We envisioned that a heteroleptic ancillary ligand combination would enable Ni-catalyzed room temperature SMCs with aryl chlorides and challenging Lewis-basic

[*] M. E. John, M. J. Nutt, J. E. Offer, J. A. Duczynski, S. A. Moggach, G. A. Koutsantonis, R. Dorta, S. G. Stewart
 School of Molecular Sciences, The University of Western Australia
 (M310), 35 Stirling Highway, Crawley, WA 6009, Australia
 E-mail: george.koutsantonis@uwa.edu.au
reto.dorta@uwa.edu.au
scott.stewart@uwa.edu.au

K. Yamazaki, T. Miura
 Division of Applied Chemistry, Okayama University, Tsushimanaka,
 Okayama 700-8530, Japan

Additional supporting information can be found online in the Supporting Information section

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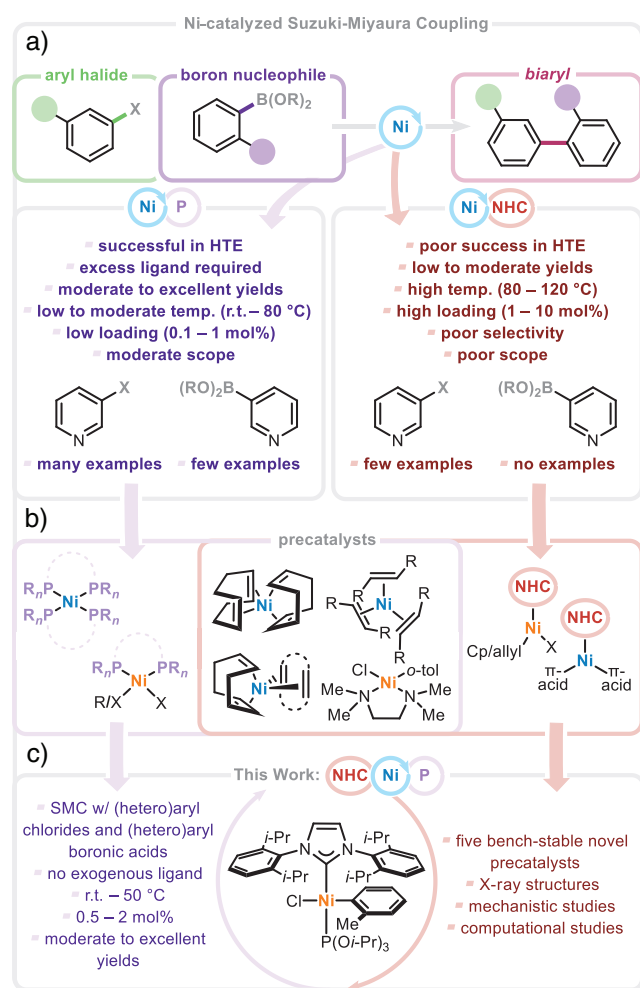


Figure 1. a) Current advantages and disadvantages of the Ni-catalyzed SMC reaction; b) A selection of air-stable nickel complexes for catalysis; c) This work: SMC reactions using Ni(NHC)[P(OR)₃](Ar)Cl as precatalysts. HTE = High-Throughput Experimentation and NHC = N-heterocyclic carbene

N-heterocycles (Figure 1c). Our group hypothesized that simultaneously employing an NHC and a phosphite (P(OR)₃) ligand would generate a system which would balance the unique kinetic and thermodynamic requirements of the Ni-catalyzed SMC. Such a system would have the advantage of using an NHC: strong σ -donation for facile oxidative addition and would remain bound to the metal throughout a catalytic cycle, thus stabilizing reactive Ni(0)/Ni(II) species. It was also anticipated that the NHC could be sterically fine-tuned to prevent off-cycle speciation, while also accelerating reductive elimination. In the case of the phosphite, we expected that the π -acidic character could provide stability to a coordinatively highly unsaturated and electron rich Ni(0) species (14e⁻, NHC-Ni-phosphite).

Beneficial ligand “synergism” between NHCs and P(OR)₃ has been reported in a variety of metal-catalyzed reactions.^[55–63] Pertinently, our group has reported an unstable Ni(0)-NHC/bis-phosphite system that showed reasonable activity in the SMC reaction.^[64] However, an

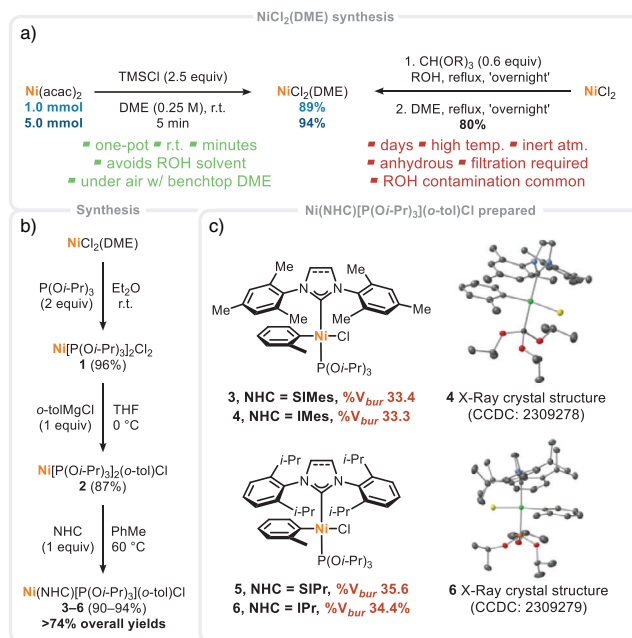


Figure 2. The synthesis and structures of Ni(NHC)[P(Oi-Pr)₃](o-tol)Cl complexes 3–6.

explicit mechanism of ligand synergism remains unrealized, as there is little evidence to strongly support any detailed mechanism or synergistic properties. In the context of this study, discrete [Ni(NHC)[P(OR)₃](Ar)X] complexes have not yet been described. An investigation into the activity of heteroleptic Ni-NHC-P(OR)₃ systems in the SMC may reveal the synergistic role of phosphorous ligands in analogous systems. Herein, we report the synthesis of four novel complexes in this class, which were successfully applied at low catalytic loadings and mild temperatures to a substantial variety of SMCs.

Results and Discussion

Catalyst Preparation

In developing a route to [Ni(NHC)[P(OR)₃](Ar)X] complexes, our group recognized that NiCl₂(DME) (DME = 1,2-dimethoxyethane) would serve as an excellent starting material. However, NiCl₂(DME) is significantly more expensive and difficult to prepare than other simple Ni(II) salts. Therefore, we developed a new synthesis of NiCl₂(DME), whereby the addition of TMSCl (2.5 equiv) to a stirring solution of Ni(acac)₂ in DME generated the desired complex in 5 min, under air, at room temperature in excellent yields (Figure 2, 89% and 94% at 1.0 and 5.0 mmol scales, respectively).

When attempting to synthesize discrete [Ni(NHC)[P(OR)₃](Ar)X] complexes, our group trialed a range of phosphite ligands [P(OEt)₃, P(Oi-Pr)₃, P(OCy)₃, P(OPh)₃, P(Ot-Bu)₃], of which triisopropyl phosphite [P(Oi-Pr)₃] proved most suitable (see Supporting Information).

NiCl₂(DME) was first treated with triisopropyl phosphite to afford the *cis*-Ni[P(O*i*-Pr)₃]₂Cl₂ complex **1** (Figure 2). Complex **1** was then treated with *o*-tolylmagnesium chloride, according to the transmetalation method of Chatt and Shaw,^[25,65] to afford Ni[P(O*i*-Pr)₃]₂(*o*-tol)Cl (**2**) in excellent yield. A substitution reaction of complex **2**, using one equivalent of free NHC, in a toluene solution at 60 °C, afforded complexes **3–6** depending on the NHC used.^[66,67] The structure of each of the nickel complexes **1–6** was unambiguously confirmed by single crystal X-ray crystallographic analysis,^[68] with IMes derived **4** and IPr derived **6** shown in Figure 2c, alongside their calculated buried volume (%V_{bur}).^[69–72]

Reaction Optimization

As (hetero)aryl chlorides are among the most commercially available aryl electrophiles, yet also one of the most challenging to couple efficiently, we selected the SMC of chlorobenzene with 4-methoxyphenylboronic acid (PMP-B(OH)₂) as a starting point for precatalyst evaluation and reaction optimization. Initial reactions conducted with **2–6** (5 mol%) at 70 °C, in ethereal solvents (1,4-dioxane or THF) showed high conversion based on crude ¹H NMR analysis. Pleasingly, no protodeborylation and only minor homocoupling were observed under these conditions. Following these promising early results, we trialed **2–6** at room temperature and reduced catalytic loading (1 and 2 mol%).^[73,74] Ni(IMes)[P(O*i*-Pr)₃](*o*-tol)Cl (**4**) and Ni(IPr)[P(O*i*-Pr)₃](*o*-tol)Cl (**6**), both bearing unsaturated NHC's, resulted in excellent conversion to the biaryl product **7**, with **6** marginally better after isolation (95%, Table 1A).

Having evaluated [Ni(NHC)[P(OR)₃](Ar)X] complexes under ideal conditions, we investigated the impact of nucleophile and base equivalents, tolerance to water, alternative solvents, and the coupling of a more challenging nucleophile with complex **6**. Reducing the stoichiometric equivalents of the nucleophile was deleterious (82%), while reducing the amount of base, to equimolar with the boronic acid, did not affect conversion. A biphasic solvent mixture (THF:H₂O) marginally reduced the conversion (85%) which is interesting as the amount of water present and stoichiometric equivalents of base often has a profoundly negative effect on Ni-catalyzed SMC reactions. The potentially green solvent 2-MeTHF gave excellent performance under our conditions. Contrastingly, however, conversions were significantly lowered when other common solvents were used (PhMe, *s*-BuOH, MTBE), potentially due to changes in base solubility. Complex **6** also efficiently coupled chlorobenzene and the electronically poor 4-trifluoromethylphenylboronic acid, to produce biaryl **8** with excellent conversion (99%). However, this combination performed poorly in 1,4-dioxane whereby the same coupling resulted in a much-diminished yield (20%). Under the optimized conditions, using reduced base equivalents, we reexamined catalysts **3–5**, with complex **4** outperforming the others (Table 1C).

In order to benchmark precatalysts **3–6** against the broader literature, we applied a wide range of other Ni

Table 1: Reaction optimization.

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a) Optimal SMC conditions with best performing Ni-NHC-P(OR)₃ complex. b) SMC optimization with **6**, biaryl **8** is 4-(trifluoromethyl)biphenyl. c) **3–5** Ni-catalysts under optimized conditions and benchmarking against other catalysts d) Optimization of SMCs for employing N-heterocyclic boronic acids. Isolated yields are in bold, reaction conversion was measured using ¹H NMR with 1,3,5-trimethoxybenzene as an internal standard.^[a] 1,4-dioxane (0.5 M).^[b] 48 h.

precatalysts to our room temperature optimized conditions. Importantly, conversions with these other Ni-systems were measured after 48 h. General Ni-precatalysts (Ni(⁴-tBu₃stb)₃, Ni(tmeda)(*o*-tol)Cl and Ni(COD)(DQ)) in combination with exogenous IPr performed poorly. Well-defined Ni-phosphine complexes [L_nNi(Ar)X], which have been reported as the

most efficient precatalysts for the Ni-catalyzed SMC, were only somewhat active under conditions (Table 1C). Interestingly, our Ni-complex **2**, precursor containing no NHC ligand, also showed some catalytic activity facilitating a 28% conversion. State-of-the-art Ni-NHC complexes, which are normally used for room temperature C–N couplings, did not generate any of the C–C coupling products.

Given the synthetic and pharmaceutical relevance of biaryl compounds containing N-heterocycles, we decided to continue our efforts toward coupling these challenging nucleophiles. Thus, we applied our optimized conditions to an SMC between chlorobenzene and 3-pyridylboronic acid. Disappointingly, trace conversion to the desired biaryl **9** was observed. Ni-catalyzed SMC employing aromatic N-heterocyclic boronic nucleophiles are especially rare, particularly with aryl chlorides. Presumably, this is because N-heterocyclic boronic nucleophiles are characteristically prone to competitive protodeborylation, catalyst ligation,^[30–35,75] and poor solubility in organic solvents. As such, state-of-the-art Ni systems typically only couple aryl bromides, boronic esters, or trifluoroborate salts, with high catalytic loading, and harsh conditions.^[76–79] To overcome these limitations, our group hypothesized that the addition of exogenous fluoride would allow us to use, milder conditions, boronic acids, low catalytic loading, and broad range of functional groups. Exogenous fluoride could inhibit protodeborylation by imposing an equilibrium between the susceptible boronic acid and the inert trifluoroborate salt. Furthermore, the boronic acid could be activated to the fluorinated boronate complex or a “transmetalation active” intermediate $[\text{Ar-Ni-F}]$ ^[77–79] could form via halide-metathesis, which could enable difficult transmetalation. TBAF has also included elsewhere as an additive, as a base or phase transfer catalyst in palladium catalyzed SMC reactions.^[80–82] In our case, with TBAF addition and slight changes in catalyst loading, temperature, and equivalents of the nucleophile, base and water, desired biaryl **9** was isolated in excellent yield (88%). To ascertain whether the phase transfer properties or fluoride were responsible for this outcome, cesium fluoride and TBAC were also trialed as additives, both of which afforded significantly lower yields (Table 1D). Presumably the phase transfer ability of the tetrabutylammonium salt is not the dominant factor in this process given that TBAC was lower yielding. Further details are contained in the [Supporting Information](#).

Substrate Scope

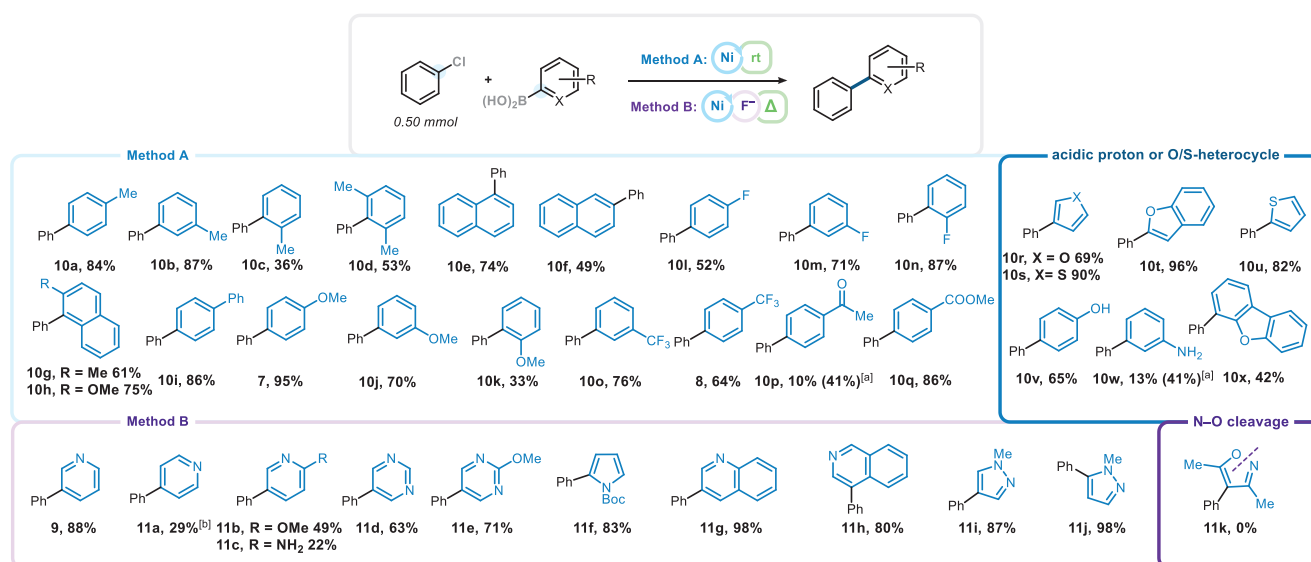
Room temperature Ni-catalyzed SMC reactions initiated using low catalyst-loading are rare in the literature and thus provided the impetus to further explore the scope of this reaction (Table 2). We were pleased to find that under these mild conditions, the electron-rich arylboronic acids afforded the coupled products in good to excellent yields. Reactions with boronic acids containing single *ortho*-substitution were generally lower yielding; however, the sterically encumbered di-*ortho*-methyl product **10d**, could be obtained in 53% yield. Likewise, the sterically encumbered naphthylboronic acids could also be coupled (to **10e**, **10g**, and **10f**). In these

examples only a small amount of protodeborylation was detected. Arylboronic acids containing electron withdrawing substituents could also be coupled with chlorobenzene. In this grouping, both CF₃ and F substituents were investigated in a range of aromatic positions relative to the boronic acid. Accordingly, products **10l–10o** and **8** were isolated in good yields. Reaction conversion with carbonyl substituted aryl boronic acid substrates varied, with the 4-acetyl derivative requiring heat, while the corresponding ester leading to **10q**, was again high yielding at room temperature.

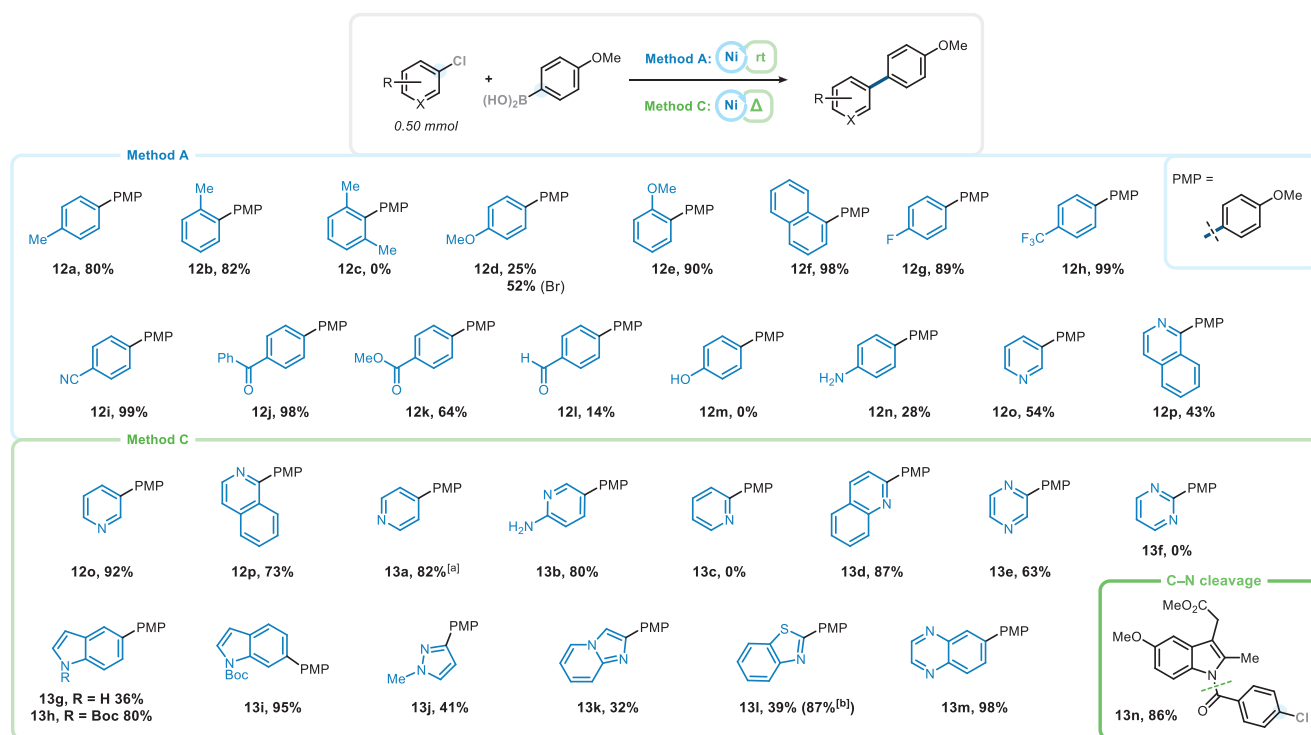
Finally, heterocyclic and arylboronic acids prone to catalyst ligation, potential side reactions, or protodeborylation were investigated. Under our conditions, the furan, benzo[*b*]furan, and thiophene(s) coupled effectively to afford the hetero-aryl products **10r–10u**.^[18] Interestingly, the phenol-boronic acid underwent coupling in good yields while the aniline required mild heating to afford **10w** in any reasonable quantity. The dibenzofuran boronic acid could also be coupled in 42% yield to **10x**. Under these conditions, coupling 5-indolylboronic acid was accompanied by some protodeborylation which could not be separated using standard chromatography (See [Supporting Information](#)).

Unfortunately, under the initial optimized conditions, the SMC reaction involving other N-heterocyclic arylboronic acids, proved challenging, however the TBAF modified protocol (Table 1D) proved successful to afford compound **9** (Method B, Table 2). The coupling of 4-pyridylboronic acid resulted in a low yield of **11a** even when the reaction was conducted at 70 °C. In contrast, aryl pyrimidines **11d** and **11e** could be prepared in good yields. The *N*-Boc-protected pyrrole boronic acid provided compound **11f** in 83% yield. The coupling of 3-chloroquinoline and 4-chloroisoquinoline provided excellent yields of **11g** and **11h** respectively. Likewise, the nitrogen-rich and *N*-methylated pyrazoleboronic acids also reacted smoothly with excellent yields (**11i** and **11j**).^[83] The reaction involving isoxazole boronic acid was unsuccessful, possibly due to N–O oxidative addition, as reported by Morandi et al.^[84] Unfortunately, the insolubility of both 2-pyridylboronic acid and 8-quinolineboronic acid in THF at 50 °C completely inhibited the coupling using these N-heterocycles. The 2-indoleboronic acid coupling was accompanied with protodeborylation as a side reaction (see [Supporting Information](#)).

Next, we turned our attention to establishing the range of aryl chlorides which could undergo the SMC with precatalyst **6** (Method A, Table 3). The coupling of 4-methoxyphenylboronic acid was high yielding with *ortho*-substituted aryl chlorides. However, comparing the yield of biaryl **12b** to **12c** suggests the more sterically hindered di-*ortho*-substituted substrates was thought to impede oxidative addition. The coupling of 4-chloroanisole was poor, however 4-bromoanisole was moderate (**12d**). The coupling of Ar–Cl electrophiles containing an electron withdrawing substituent was excellent in the case of the nitrile **12i** and benzophenone **12j** while the ester **12k** was isolated in somewhat more moderate yield (64%). The coupling of 4-chlorobenzaldehyde was poor, possibly due to competing oxidative addition of the C (acyl)–H bond of the aldehyde^[85] or simple η^2 Ni-aldehyde binding. Of the more challenging substrates trialed under

Table 2: Scope of Arylboronic Acids and Heteroarylboronic Acids and in SMC using Precatalyst **6** and Chlorobenzene.

Method A: **6** (1 mol%), chlorobenzene (0.5 mmol), boronic acid (0.75 mmol), K₃PO₄·H₂O (0.75 mmol), THF (1 mL), room temperature, 24 h. **Method B:** **6** (2 mol%), chlorobenzene (0.5 mmol), N-heterocyclic arylboronic acid (1.0 mmol), K₃PO₄·H₂O (1.0 mmol), TBAF (0.75 mmol), THF (1.75 mL), H₂O (1 mL), 50 °C, 24 h. ^[a]50 °C. ^[b]70 °C.

Table 3: Scope of Aryl Chlorides and Heteroaryl Chlorides in SMC using Precatalyst **6** and 4-Methoxyphenylboronic acid.

Method A: **6** (1 mol%), aryl chloride (0.5 mmol), 4-methoxyboronic acid (0.75 mmol), K₃PO₄·H₂O (0.75 mmol), THF (1 mL), room temperature, 24 h. **Method C:** **6** (1 mol%), (hetero)aryl chloride (0.5 mmol), 4-methoxyboronic acid (0.75 mmol), K₃PO₄·H₂O (0.75 mmol), THF (1 mL), 50 °C, 24 h. ^[a]Coupled as the pyridine·HCl salt. ^[b]**6** (2 mol%).

these conditions, the phenol **12m** could not be prepared, while the aniline derived **12n** could only be produced in 28% yield. Substrates 3-chloropyridine and 2-chloroisoquinoline also underwent a SMC reaction under these mild conditions, to yield **12o** and **12p**, in moderate yields.

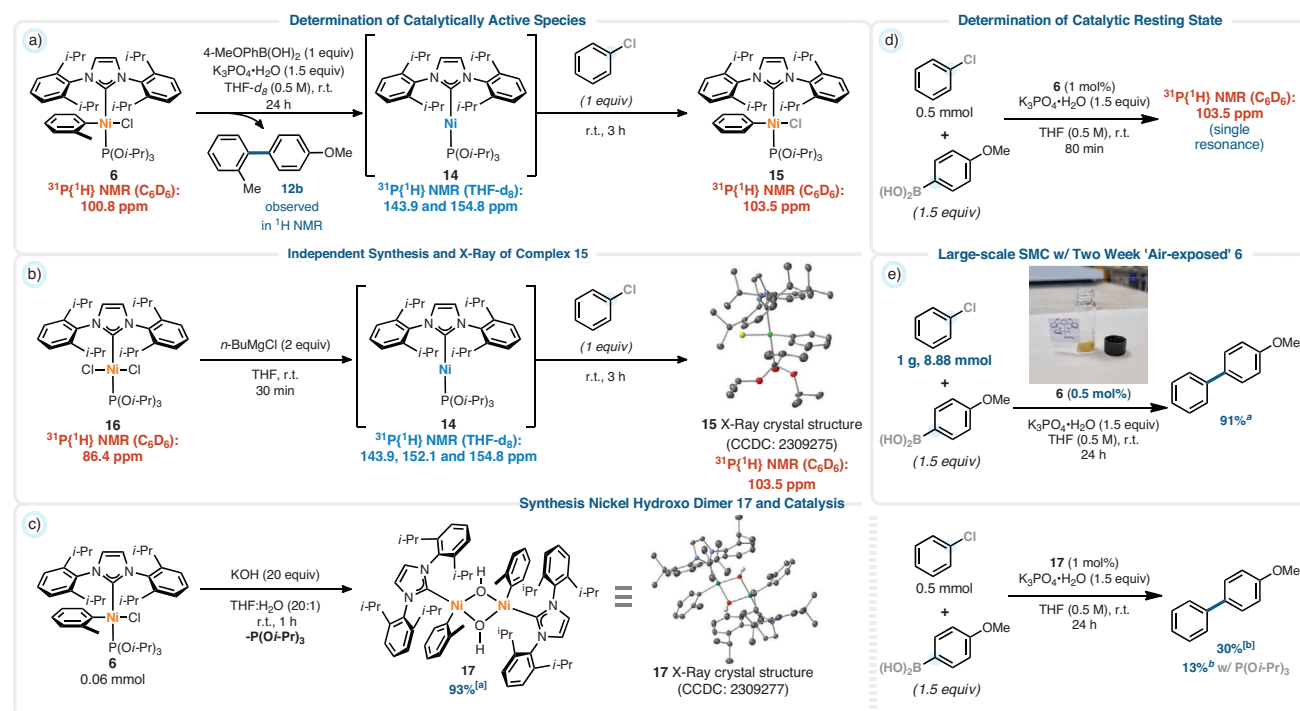
Given the unsatisfactory conversion rates of several N-heterocyclic chlorides at room temperature, we proceeded to further investigate the reaction scope at 50 °C (Method C, Table 3). To our delight, conducting the coupling of 3-chloropyridine under mild heating (50 °C) improved the yield of **12o** from 54% to 92%. Similarly, the reaction involving 2-chloroisoquinoline was also improved to yield 73% of **12p** at this slightly higher temperature. We found, under these revised conditions, that using the HCl salt of 4-chloropyridine was required to enable a good conversion to **13a** (82%). 2-Chloropyridine as a substrate failed to react, presumably reflecting what has been described as the “2-pyridyl organometallic cross-coupling problem”^[86,87] with concomitant production of catalytically inactive dimeric nickel species.^[88,89] Quinoline **13d** could be prepared under these conditions from the corresponding heteroaryl chloride. Interestingly, the chloropyrazine underwent coupling to **13e**, while the 2-chloropyrimidine did not react under our conditions, possibly due to its basicity. The *N*-Boc protected indoles **13h** and **13i** along with **13p** were produced in excellent yields. The coupling of N-heteroaryl chlorides trialled including 5-chloroindole, 2-chloroimidazo[1,2-*a*]pyridine, and 2-chlorobenzothiazole afforded low yields of the heteroaryl-aryl products using 1 mol% loading of precatalyst. These results suggest that poisoning of the catalyst may be occurring in these cases due to the Lewis basic nature of the substrates. Repeating the reaction of 2-chlorobenzothiazole with 2 mol% of catalyst resulted in an 87% yield of **13l**, indicating that either higher loading or further reaction optimization is required for such examples. A catalyst limitation was realized from the attempted reaction of indomethacin, where cleavage of the amide moiety occurred to give the deacylated indole **13n** as the sole product (See [Supporting Information](#)). Furthermore, coupling with other substrates bearing either primary or *N,N*-dimethyl amide substituents also failed, again suggesting Ni-catalyzed C–N bond cleavage. This is unsurprising, given the precedent for similar Ni-catalyzed C–N bond cleavage-promoted transformations in the literature.^[13,90]

Mechanistic Considerations

To identify the catalyst resting state and the structures of catalytically relevant species, we conducted a series of reactions with precatalyst Ni(IPr)[P(Oi-Pr)₃](*o*-tol)Cl (**6**) which were monitored by ³¹P{¹H} and ¹H NMR spectroscopy. The first reaction attempted to elucidate the products of the endogenous activation process of precatalyst **6**. Here a stoichiometric amount of 4-methoxyphenylboronic acid in the presence of 1.5 equivalents of base was stirred at room temperature (Scheme 1a, See [Supporting Information](#) for further details). ¹H NMR resonances attributable to biaryl **12b**^[38] were observed, presumably resulting from transmetalation and subsequent reductive elimination.^[23]

As the conversion to biaryl **12b** was high, we tentatively excluded comproportionation to Ni(I) species, as observed in nickel systems featuring chelating diphosphines.^[91] ³¹P{¹H} NMR monitoring of this reaction indicated the appearance of two key resonances at 143.9 and 154.8 ppm (THF-*d*₈). These clear downfield signal shifts are strongly indicative of Ni(0) species forming and are reminiscent of the recorded values for Ni(NHC)[P(Oi-Pr)₃]₃(L) species (L = THF, NHC wingtip/backbone),^[64] and the palladium(0) analog Pd(IPr)[P(Oi-Pr)₃] (155.9 ppm).^[92] Indeed, when this mixture presumably containing Ni(IPr)[P(Oi-Pr)₃] (**14**), was subsequently treated with chlorobenzene at room temperature, a yellow-colored solution was formed, corresponding to a ³¹P{¹H} NMR spectrum with a single resonance at 103.5 ppm (C₆D₆), which can be attributed to the oxidative addition product **15**. A second synthetic pathway was proposed to confirm and support the existence of both the tentatively assigned Ni(0) 14e[−] species **14** and validate the structure of complex **15** (Scheme 1b). Treating Ni(IPr)[P(Oi-Pr)₃]Cl₂ **16** with *n*-BuMgCl (2.0 equiv)^[8,9] at room temperature immediately resulted in a red-colored solution. ³¹P{¹H} NMR analysis (THF-*d*₈) of this mixture again resulted in the observation of downfield resonances at 143.9 and 154.9 ppm, similar to those observed previously (Scheme 1a), and a large signal at 152.0 ppm. Treatment of this solution with chlorobenzene for 3 h at room temperature afforded **15** as the major product, as characterized by ¹H and ³¹P{¹H} NMR spectroscopy. Finally, following crystallization, an X-ray crystallographic analysis unambiguously confirmed the structure of **15**. The above experiments strongly suggest the involvement of Ni(IPr)(P(Oi-Pr)₃) (**14**) and related Ni(NHC)[P(Oi-Pr)₃](L) and the oxidative addition product **15** represents the resting state species in the SMC.

Dimeric Ni-μ-hydroxo-complexes [Ni(Ar)(μ-OH)(PR₃)₂]₂ have been reported to be either directly involved in the transmetalation step or to exist as off-cycle species.^[30,35,93,94] Such dimeric Ni-μ-hydroxo complexes are conceivably also involved in the SMC using our Ni(NHC)[P(OR)₃](Ar)X precatalysts **3–6**, as reactions were performed in the presence of residual water from K₃PO₄·H₂O. To examine this possibility, an authentic sample of a nickel-hydroxo complex was prepared by treating precatalyst **6** with excess KOH in a water/THF mixture at room temperature (Scheme 1c). Following a short mixing period and appropriate workup, a bright yellow precipitate containing [Ni(IPr)(μ-OH)(*o*-tol)]₂ **17** was obtained (93% yield). The absence of resonance in the ³¹P{¹H} NMR spectrum confirmed the loss of P(Oi-Pr)₃, and the structure of **17** was unambiguously ascertained by single crystal X-ray crystallographic analysis. A catalytic amount of this hydroxo-bridged dimer **17** (1 mol%) was then used in an SMC between chlorobenzene and 4-methoxyphenylboronic acid, resulting in a clearly lower yield of the biaryl product **7** (30%, Scheme 1c). The same reaction conducted in the presence of triisopropyl phosphite led to a further erosion of yield giving **7** in 13% (isolated). These observations suggest that dimer **17** is unlikely to be an integral part of the catalytic cycle. Furthermore, it is also improbable that **17** is a resting state intermediate for an active monomeric hydroxo-species Ni(NHC)[P(Oi-Pr)₃](Ar)OH that contains the phosphite



Scheme 1. Mechanistic and catalyst stability studies. a) Stepwise reactions to identify biaryl **12b** by ^1H NMR spectroscopy and complexes **14** and **15** by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy; b) Synthesis of **14** and **15** from **16**; c) Synthesis of nickel hydroxo dimer **17** and standard SMC using nickel hydroxo dimer **17** with/without $\text{P}(\text{O}i\text{-Pr})_3$; d) Standard SMC monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy; e) Large-scale SMC using **6** which had previously undergone two-week air exposure. [a] Isolated yield is reported. [b] NMR conversion is reported from 1,3,5-trimethoxybenzene internal standard. For solid-state structures of **15** and **17**, thermal ellipsoids are displayed at 50% and have hydrogens omitted for clarity.

ligand.^[23,93,94] To substantiate these hypotheses, a reaction using precatalyst **6** (1 mol%), 4-methoxyphenylboronic acid and chlorobenzene was also monitored using $^{31}\text{P}\{^1\text{H}\}$ NMR, C_6D_6 (Scheme 1d). Over a period of 80 min the resonance attributed to the bound phosphite within **6** (100.8 ppm) reduced in intensity and was replaced by a new single resonance at 103.5 ppm (as in **15**) without large quantities of free phosphite being observed. A final study on the influence of free phosphite on the reaction yield revealed that an additional 1 mol% $\text{P}(\text{O}i\text{-Pr})_3$ had no influence on the SMC reaction yield but that 10 mol% significantly deteriorated the yield (See Supporting Information for details). Given that oxidative addition product **15** appears to represent the resting state species of our catalytic cycles, these last two experiments, while pointing toward a mechanism that retains $\text{P}(\text{O}i\text{-Pr})_3$ throughout the cycle, cannot exclude an alternative scenario where the phosphite is not constantly bound to the catalyst.

Lastly, to determine the stability of our precatalyst, a solid sample of **6** was taken outside the glovebox and placed open to the air for two weeks (Image, Scheme 1e). $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of this sample showed the typical resonance at 100.8 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra with no signs of degradation of the catalyst. Similarly, the ^1H NMR spectra were identical before and after exposing **6** to oxygen and humidity. This air-exposed sample was then used to catalyze a gram-scale reaction between chlorobenzene (8.88 mmol) and 4-methoxyphenylboronic acid (catalyst 0.5 mol%) yielding 91% of 4-phenylanisole **7**.

Computational Study

We decided to study the mechanism using computational analysis to elucidate the reaction process further. Density functional theory (DFT) calculations were performed using SMD(THF)/M06/def2-TZVP//SMD(THF)/B3LYP-D3/def2-SVP level of theory on a SMC under a classical Ni(0)/Ni(II) mechanism consisting of oxidative addition / transmetalation / reductive elimination sequence. Having made the observations from the practical measurements, we hypothesized the following mechanism (Figure 3). Initially, the nickel precatalyst **6** undergoes transmetalation and reductive elimination to generate the catalytically active Ni(0) species **14**.^[23–35] Then, a ligand exchange process occurs with aryl chloride (η^2) to afford **Int1**.^[94] An oxidative addition allows for the generation of the Ni(II) intermediate **Int2**, through the transition state **TS1**, with an activation energy barrier of 9.5 kcal mol^{−1}. Coordination of free phosphite to **Int2** allows for the off-cycle formation of the resting state species **15**. The formation of **15** could also proceed through oxidative addition of **14**; however, this pathway has a large energy barrier of 29.4 kcal mol^{−1} through the transition state **TS1'** and thus we propose the lower energy pathway through **Int1**. Next, we propose ligand exchange between chloride and boronic acid with potassium phosphate to give the intermediate **Int3**.^[95–97] Transmetalation from **Int3** leads to the Ni(II) diaryl intermediate **Int4**.^[98,99] Given the computed barrier of **TS2** was 15.6 kcal mol^{−1}, we

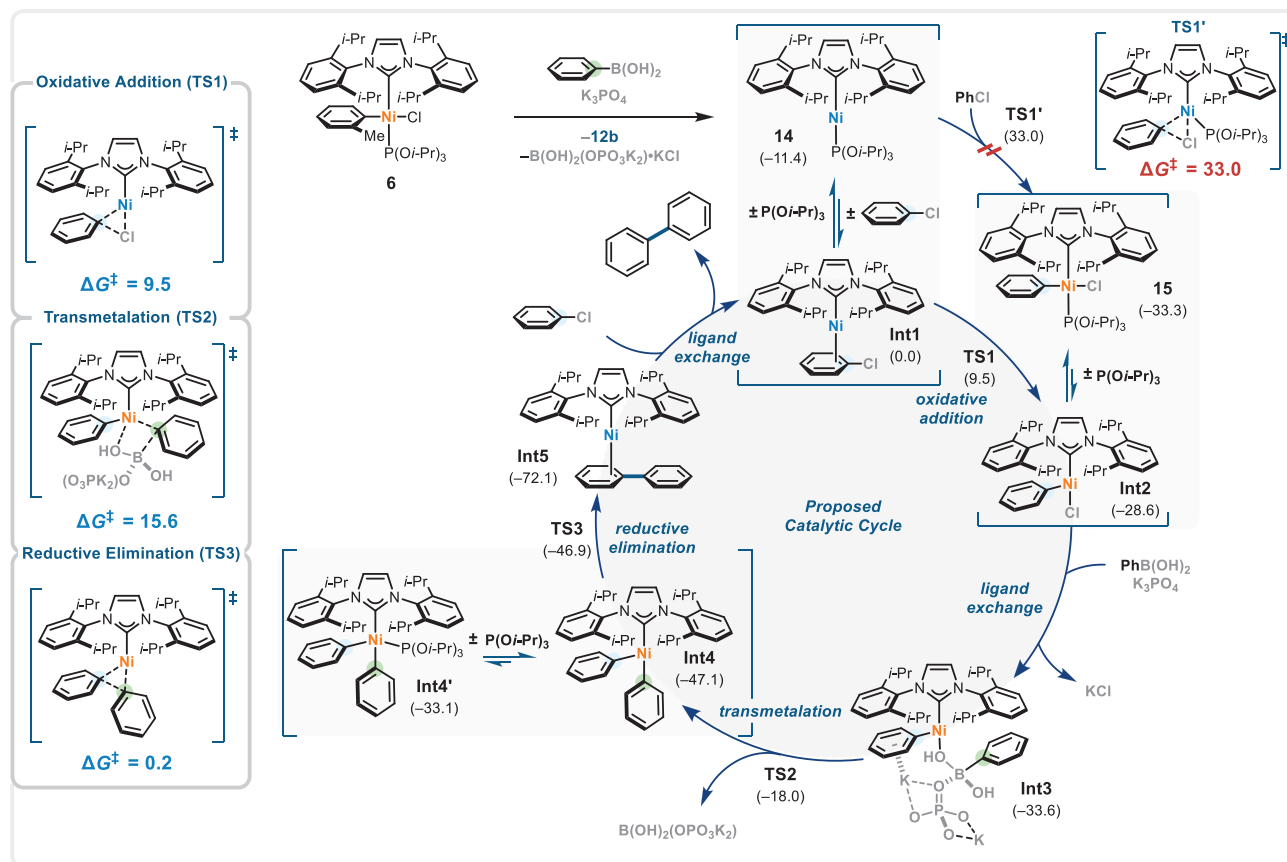


Figure 3. Proposed catalytic cycle (ΔG [kcal mol⁻¹]) of the Ni-catalyzed Suzuki-Miyaura cross-coupling between aryl chlorides and arylboronic acids using **6**; All DFT calculations were performed at SMD(THF)/M06/def2-TZVP//SMD(THF)/B3LYP-D3/def2-SVP level of theory.

suggest that this transmetalation is the rate-determining step. Phosphite binding at this stage would afford **Int4'** which is thermodynamically less stable. A facile reductive elimination of **Int4** to give **Int5** proceeds almost barrierless. Ligand exchange of **Int5** furnishes the cross-coupled product and regenerates **Int1**. For further discussion on the stabilization^[100–102] of **Int2** to **Int2'** using phosphite or other ligands and the investigation of transmetalation steps, through a Ni-hydroxide complex or fluoride *trans*-halogenation, please see [Supporting Information](#).

Conclusion

In summary, the first series of Ni(II) complexes of the general formula Ni(NHC)[P(OR)₃](*o*-tol)Cl have been described. The catalytic properties of Ni(IPr)[P(O*i*-Pr)₃](*o*-tol)Cl (**6**) was explored to prepare a variety of biaryls through the SMC between aryl chlorides and aryl boronic acids. The reaction could be carried out with low catalytic loading (0.5–2 mol%) at room temperature or under mild heating. This novel precatalyst could also be used in presence of TBAF, generating a catalytic system that facilitates a SMC reaction between aryl chlorides and N-heterocyclic boronic acids. The precatalyst **6** as a solid was found to be air-stable, amenable to

larger scale reactions and can be used in the green solvent 2-MeTHF. Importantly, the activity of this Ni(NHC)[P(OR)₃] system, and our computational investigation, supports the theory that successful Ni-catalyzed SMC systems require thermodynamically stable L₂Ni and kinetically accessible L₁Ni species, which may explain the inefficiency of previous Ni(NHC) systems in this reaction. Additionally, this investigation also revealed that the beneficial “synergy” in heteroleptic systems, at least in Ni SMC, arises from the formation of a stable off-cycle species, that inhibits the decomposition of the catalytically active species. Overall, the broad substrate scope and functional group tolerance of the present system will be valuable for both academic and industrial pursuits to gain access to molecular scaffolds that are abundant in fine chemicals and pharmaceuticals. Further studies of other types of cross-coupling reactions using these Ni(NHC)[P(OR)₃](Ar)Cl precatalysts are currently underway in our laboratory.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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