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Stable Nickel(0) Phosphites as Catalysts for C–N Cross-Coupling Reactions

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Abstract: Herein we describe the design and preparation of inexpensive, air-stable nickel phosphite-based catalysts for use in the C–N cross-coupling reaction. The combination of nickel tetrakis(triphenyl phosphite) {$Ni[P(OPh)_3]_4$} and 1,1′-bis(diphenylphosphino)ferrocene (dppf), and in particular a newly developed catalyst $(dppf)Ni[P(OPh)_3]_2$, were found to be extremely effective in catalyzing a range of amination reactions of anilines and amines with aryl chlorides. This new catalyst system offers an alternative to the bis(cyclooctadienyl)nickel [$Ni(COD)_2$] and palladium(0) catalysts commonly used for C–N bond formation.

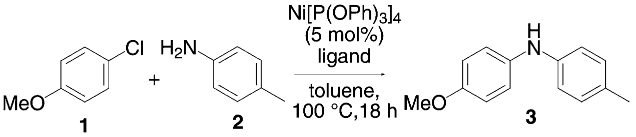
Keywords: catalyst design; C–N bond formation; cross-coupling; nickel phosphites

Nickel catalysis is increasingly being used in cross-coupling chemistry as a reactive and cost effective alternative to palladium catalysis. Nickel catalysts have many advantages for cross-coupling reactions including lower energy barriers for oxidative addition, allowing a wider range of leaving groups.[1] Although Ni(II) catalysts are generally air-stable, they often require an additional reducing agent. Unfortunately, in many instances, zero-valent nickel catalysts suffer from instability or low reactivity. In many cross-coupling reactions, $Ni(COD)_2$ has been used as pre-catalyst in combination with other ligands such as phosphines[2,3] or N-heterocyclic carbenes (NHC).[4–7] In particular, several groups have used $Ni(COD)_2$ in combination with dppf in reactions such as the Heck,[8,9] Suzuki[10] and Buchwald–Hartwig[5,11–13] reactions. Furthermore, this combination of pre-catalysts and ligands has been recently used in reactions involving C–H functionalization.[14,15] Hartwig and co-workers fine-tuned the reactivity of this system through extensive modifications to the dppf ligand.[16,17] Additionally, the combination of $Ni(COD)_2$ with other bidentate ligands has also been examined by several groups.[18–20] Although the use of $Ni(COD)_2$ has numerous benefits, this pre-catalyst has the drawbacks of being highly air-sensitive, difficult to transport, costly and difficult to prepare.

Alternatives to the $Ni(COD)_2$ and phosphine catalytic system for C–N cross-coupling reactions have also been investigated using either Ni(0) or Ni(II) as precatalysts.[21,22] Some of these reactions require strong bases and other additives such as Zn.[23] Nickel NHC complexes, heterogeneous nickel catalysts and nickel in combination with other metals (Cu and Ni oxide/C) have also been examined.[24–29] Previously, nickel phosphite complexes have been used in Heck cross-coupling reactions; however, the substrate scope was not fully established and catalyst exploration was limited.[30] Ni(II) in the form of $Ni(OAc)_2{\cdot}4H_2O$ has been used previously in combination with phosphites in aminocarbonylation reactions with DMF.[31] Ni(0) phosphite complexes are cheaper and more air-stable than $Ni(COD)_2$[32,33] and nickel phosphine complexes. Furthermore, simple nickel phosphites have been used in other unrelated processes such as promoting the reaction of allylic acetates[34] with thiols and in hydrocyanation reactions.[35,36]

Ideally, the nickel phosphite complex used for catalysis would be in the nickel(0) oxidation state, readily dissociate the phosphite ligands, thus providing a future stable alternative for $Ni(COD)_2$. Such Ni(0) species could also potentially be used in combination with other ligands to initiate cross-coupling reactions. Our exploration of phosphites as supporting ligands in catalysts or precatalysts began with an examination of $Ni[P(OPh)_3]_4$, which can be prepared in one step from inexpensive nickelocene.[37] When $Ni[P(OPh)_3]_4$ (5 mol%) was combined with (*R,S*)-BINAP, the re-

Table 1. Ligand-based screening of Ni[P(OPh)$_3$]$_4$-catalyzed C–N coupling between *para*-chloroanisole **1** and *para*-toluidine **2**.

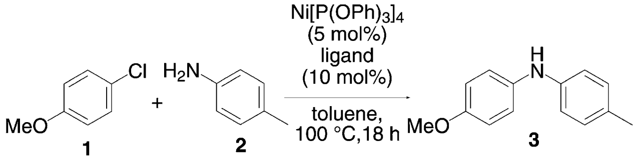


Entry	Ligand[a]	GC conv.[b] [%]	Yield [%]
1	(*R,S*)-BINAP (5 mol%)	70	53
2	(*R,S*)-BINAP (10 mol%)	84	66
3	Ad$_2$PBu (10 mol%)	<1	n.d.
4	XantPhos (5 mol%)	26	n.d.
5	XPhos (10 mol%)	<1	n.d.
6	dppe (5 mol%)	<1	n.d.
7	dppf (10 mol%)	76	68
8	1,10-phen (10 mol%)	1	n.d.
9	TMEDA (10 mol%)	1	n.d.
10	DavePhos (10 mol%)	<1	n.d.
11	(*R,S*)-BINAP (5 mol%)	70	53

sulting species catalyzed the reaction between *para*-chloroanisole **1** and *para*-toluidine **2** to afford the amine **3** in 53% yield (Table 1, entry 1). Moreover, we were encouraged to observe that the yield of **3** increased to 66% upon increasing the phosphine content to 10 mol% (entry 2).[19] Unfortunately, little or no product was obtained when **1** and **2** were reacted in the presence of other monodentate and bidentate phosphines including Ad$_2$PBu, dppe, DavePhos and XPhos. The proof of concept of a phosphite-based catalyst for C–N coupling reactions was further confirmed when dppf was used (entry 7), providing amine **3** in 68% yield.

Given the success of the combination of Ni[P(OPh)$_3$]$_4$ and dppf (entry 7), and recent reports on the use of dppf in C–N cross-coupling reactions,[11] we decided to briefly investigate other bases and another phosphite complex, Ni[P(OEt)$_3$]$_4$ (Table 2). Unfortunately altering the type of base did not significantly improve the yield. Additionally, the inactivity of Ni[P(OEt)$_3$]$_4$ (entry 5) supported previous reports of low lability of ethyl phosphites in zerovalent nickel complexes.[38] Varying the amounts of phosphine and nickel, and their ratio, seemed to have a slightly deleterious effect on the reaction (entries 8–10). Interestingly, the presence of an additional phosphite seemed

Table 2. Catalytic conditions in the C–N cross-coupling between *para*-chloroanisole **1** and *para*-toluidine **2**.



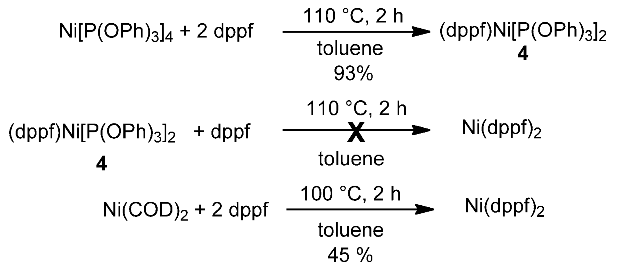
Entry	Catalyst	Ligand	Base[a]	GC conv.[b] [%]	Yield [%]
1	Ni[P(OPh)$_3$]$_4$	dppf	NaO-*t*-Bu	76	68
2	Ni[P(OPh)$_3$]$_4$	dppf	NaH	20	18
3	Ni[P(OPh)$_3$]$_4$	dppf	NaH[c]	78	30
4	Ni[P(OPh)$_3$]$_4$	dppf	KHMDS	7	n.d.
5	Ni[P(OEt)$_3$]$_4$	dppf	NaO-*t*-Bu	0	0
6	Ni[P(OPh)$_3$]$_4$	dppf + P(OPh)$_3$	NaO-*t*-Bu	39	n.d.
7	Ni[P(OPh)$_3$]$_4$	dppf	NaO-*t*-Bu[c]	72	52
8	Ni[P(OPh)$_3$]$_4$	dppf (5 mol%)[d]	NaO-*t*-Bu	59	47
9	Ni[P(OPh)$_3$]$_4$ (10 mol%)[d]	dppf	NaO-*t*-Bu	40	n.d.
10	Ni[P(OPh)$_3$]$_4$ (2 mol%)[d]	dppf (4 mol%)	NaO-*t*-Bu	32	n.d.
11	Ni[P(OPh)$_3$]$_4$	D-*t*-BuPF	NaO-*t*-Bu	0	0
12	Ni[P(OPh)$_3$]$_4$	DCyPF	NaO-*t*-Bu	69	66
13	Ni[P(OPh)$_3$]$_4$	D-*i*-PrPF	NaO-*t*-Bu	75	65
14	Ni[P(OPh)$_3$]$_4$	*p*-CF$_3$-dppf	NaO-*t*-Bu	59	50
15	Ni[P(OPh)$_3$]$_4$	*p*-OMe-dppf	NaO-*t*-Bu	75	61

[a] In each case 1.4 equiv. of NaO-*t*-Bu were used.

[b] Monitored by GC only promising candidates were subjected to work-up and isolation.

[c] 3 equiv. of base were used.

[d] Modified mol% used; DCyPF = 1,1′-bis(dicyclohexylphosphino)ferrocene, D-*t*-BuPF = 1,1′-bis(di-*tert*-butylphosphino)ferrocene; D-*i*-PrPF = 1,1′-bis(diisopropylphosphino)ferrocene; *p*-CF$_3$-dppf = 1,1′-bis[di(4-trifluoromethylphenyl)phosphine]ferrocene; *p*-OMe-dppf = 1,1′-bis[di(4-methoxyphenyl)phosphine]ferrocene.



Scheme 1. Reactions of Ni(0) precursors with dppf.

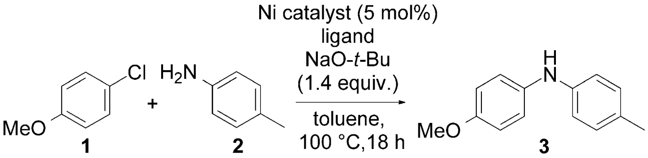
only to hinder the cross-coupling process (entry 6), possibly because of an effect on the phosphine dissociation equilibrium. Finally, inspired by previous reports by Hartwig on dppf derivatives and palladium-catalyzed C–N cross-couplings, we examined small changes to the dppf ligand that slightly altered the electronics.[16,17] Use of the dppf derivatives, entries 11–15 (Table 2), only moderately affected the yield of the amination reaction. However, given the additional synthetic requirements of these ligands, this line of inquiry was concluded.

The combination of $Ni[P(OPh)_3]_4$ and dppf provided the best catalytic conditions, and hence we focused on identifying the exact catalytic species implicated in this reaction. Moreover, we sought to compare our system with that studied in the seminal work of Buchwald and co-workers on an $Ni(COD)_2$/dppf-catalyzed reaction.[11] Our nickel phosphite example was lower yielding, however, the potential to form $Ni(dppf)_2$ through the use of either $Ni(COD)_2$ or $Ni[P(OPh)_3]_4$ as pre-catalysts was evident. We targeted this species from both sources, $Ni(COD)_2$ and the nickel phosphite tetrakis complex, $Ni[P(OPh)_3]_4$. $Ni(COD)_2$ reacted readily with dppf to afford $Ni(dppf)_2$; however the reaction of $Ni[P(OPh)_3]_4$ with dppf (toluene, 100 °C) yielded only $dppfNi[P(OPh)_3]_2$ **4** (Scheme 1).

Attempts to force the substitution (toluene, 100 °C) of the remaining phosphite ligands proved fruitless. The similarity of these conditions to our C–N cross-coupling conditions suggest that $Ni(dppf)_2$ may not be involved in the early stages of the reaction. Given that either $Ni(COD)_2$ or complex **4** could be considered as putative catalysts or precatalysts in the amination reaction studied here, they were both subjected to these reaction conditions (Table 3). The coupled secondary amine was successfully produced in the system catalyzed by the bis-dppf nickel complex (entry 3) and likewise in the presence of the mono dppf phosphite system **4** (entry 4).

These findings indicate that the steric hindrance about the metal center in $Ni(dppf)_2$ is not sufficient to obstruct coordination of incoming coupling partners. Interestingly, the $(dppf)Ni[P(OPh)_3]_2$ system (**4**) in combination with additional dppf (5 mol%), as an additive, produced the amine product in a yield that was comparable to that obtained using the combination of $Ni(COD)_2$ with dppf (entry 2).

Table 3. Investigation of precatalysts and catalytic species containing dppf.



Entry	Catalyst	Ligand	GC [%]	Yield [%]
1	$Ni[P(OPh)_3]_4$	dppf (10 mol%)	76	68
2	$Ni(COD)_2$	dppf (10 mol%)	99	84
3	$Ni(dppf)_2$	–	67	59
4	$(dppf)Ni[P(OPh)_3]_2$	–	77	61
5	$(dppf)Ni[P(OPh)_3]_2$	dppf (5 mol%)	94	82
6[a]	$(dppf)Ni[P(OPh)_3]_2$	dppf (5 mol%)	0	0

[a] Reaction was performed in non-inert conditions.

The higher yield obtained in the system with added dppf (entry 5) compared to **4** alone (entry 4) suggests that the additional dppf assists in a specific step in the C–N cross-coupling catalytic cycle. We found that **4** (Figure 1) is air-stable in the solid form, unlike its Ni(0) counterpart $Ni(COD)_2$.[33] Unfortunately, this system was not effective under non-inert conditions. (entry 6). Very recently, during the final stages of this study, a similar air-stable catalytic system [(dppf)Ni(*o*-tolyl)Cl] was reported that also affords higher yields if dppf is added.[39]

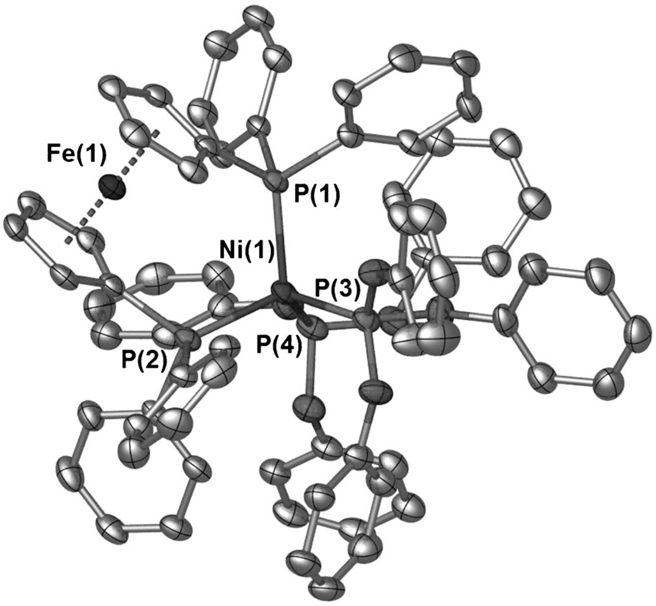
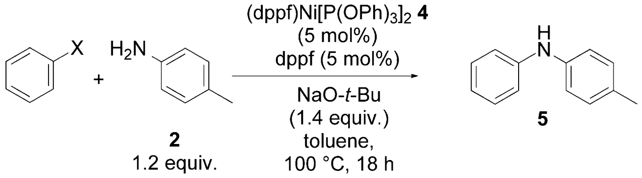


Figure 1. Molecular representation of the ORTEP structure of $(dppf)Ni[P(OPh)_3]_2$ **4**. Hydrogen atoms have been removed for clarity.

Table 4. Catalyst **4** and C–N cross-coupling of various functionalized aryl species with *para*-toluidine **2**.



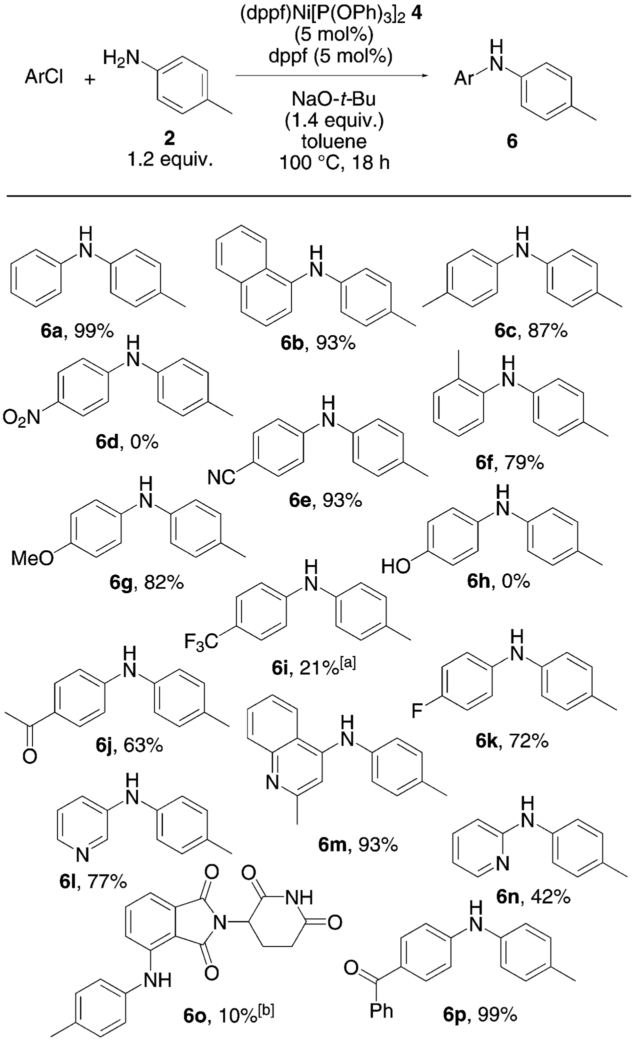
Entry	X	Yield [%]	Entry	X	Yield [%]
1	Cl	99	5	OTs	47
2	Br	100[a]	6	$OCOCH_3$	0
3	I	100[a]	7	$OCOCF_3$	0
4	OTf	56	8	OCH_3	0

[a] GC conversion.

The amination compatibility of various substituted aryl substrates containing diverse leaving groups has previously been reported for a range of simple to complex nickel catalysts.[5,40] To test the catalytic ability of (dppf)Ni[P(OPh)$_3$]$_2$ (**4**), we examined the C–N cross-couplings of a range of halides and pseudohalides with *para*-toluidine (**2**) (Table 4). Interestingly, there seemed to be no drop off in reactivity across the halides surveyed, possibly due to the excellent oxidative addition ability of the complex. By contrast, the yields obtained for the aryl triflate and less commonly reported aryl tosylate were both modest. However, more elaborate leaving groups used successfully in previous work, were not reactive in this system.[2,41–44]

Next we surveyed the catalytic ability of (dppf)Ni[P(OPh)$_3$]$_2$ (**4**) in the cross-coupling reactions of a range of aryl chlorides with **2** (Table 5). No correlation could be discerned between the electronics of the aryl chloride and the yield, with reactions involving chloroanisole (leading to **6g**) and chlorobenzophenone, (producing **6p**) both providing high yields. The substitution pattern of a methyl substituent in the coupling partner was determined to affect the yield slightly, with lower yields obtained for products with the methyl group in the *ortho* position (**6f**). The reaction did not proceed in the presence of a nitro substituent (**6d**), a phenomenon also recently observed in nickel-mediated Heck cross-coupling reactions.[9] In the two pyridyl-derived substrates tested moderate to good results were observed, depending on the position of the nitrogen (**6l** and **6n**). The quinoline derivative **6m** could also be prepared successfully in 93% yield.[45] To determine if the catalyst would function on more complex ring systems, a thalidomide derivative was also prepared (**6o**). Although this conversion was achieved in low yields, large amounts of the starting aryl chloride were also found remaining.[46]

Table 5. Scope of the aryl chloride coupling partner.

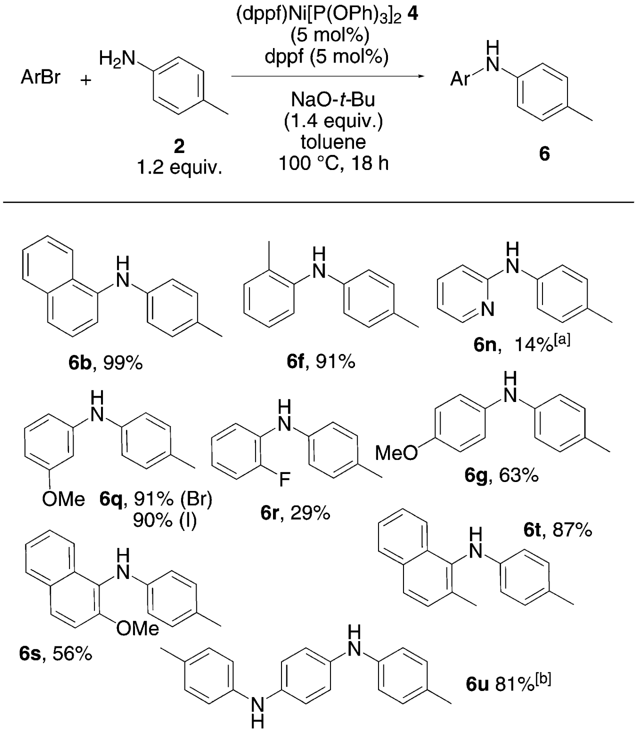


[a] 40 h, an aliquot was taken after 18 h and showed 21% GC conversion.

[b] NMR yield.

Following the success of the aryl chlorides a small reaction trial was performed with a range of aryl bromides (Table 6). In this case there seemed to be no discernable reactivity pattern or predictable change in activity when compared to the corresponding aryl chlorides. Compound **6b** and **6f** were produced in higher yields (99% and 91%, respectively), but the methoxy-substituted compound **6g** was prepared in a slightly lower yield of 63%. Interestingly, the reaction leading to **6n** underwent a second C–N coupling to afford a bis-pyridyl compound. The differences in the aryl halide leading to product **6q** had no effect on the yield. The remaining aryl bromides resulted in good conversions to the secondary amines, except in the case of the fluorinated derivative **6r**. The reaction of 4-bromochlorobenzene with aniline **2** resulted mainly in the formation of the 1,4-benzenediamine derivative **6u** (81%), whearas the monocoupled deriv-

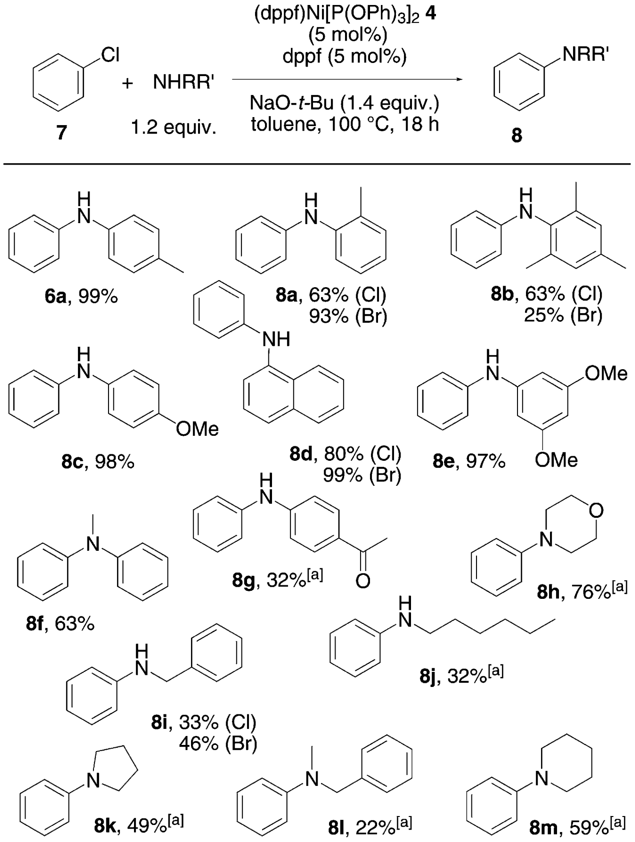
Table 6. Scope of the aryl bromide coupling partner.



[a] In this instance a large amount of the bis-pyridyl aniline was also produced (83%, NMR yield), please see the Supporting Information.

[b] Compound resulted from competing experiment with 4-bromochlorobenzene at 60 °C for 22 h.

Table 7. Scope of the amine coupling partner for the amination reaction.



[a] 5 mol% (*R,S*)-BINAP was used.

atives were only isolated in a total of 7% yield (3:2 favoring the Ar–Br coupled product).

The range of amines suitable for this reaction was also explored (Table 7). Using (dppf)Ni[P(OPh)$_3$]$_2$ (**4**) as a catalyst, the slightly hindered aniline **8b** bearing two methyl substituents in an *ortho* configuration was successfully obtained, although in moderate yield. The two electron-rich anilines **8c** and **8e** were each obtained in a high yield, as was the naphthylamine substrate **8d**. The secondary aniline leading to **8f** was coupled in 63% yield. However, coupling of the benzylamine was poorer even when the more reactive aryl bromide was used to afford **8g**. The coupling of morpholine was successful in 76% yield, but more so when (*rac*)-BINAP was used as an additive instead of dppf or when additional catalyst was used. This alternate phosphine additive was also preferentially used for the coupling of other secondary amines leading to products **8k**, **8l** and **8m**. The coupling of the primary amine to produce compound **8j** was also moderately successful. Such amines have very recently been formed through a (BINAP)Ni(η^2-NC–Ph) complex-catalyzed reaction.[47]

An early insight into the reaction's catalytic cycle was attempted through the monitoring of the reaction by ^{31}P NMR spectroscopy (see the Supporting Information). In the early stages of the reaction, it is clear the catalyst **4** is consumed with the disappearance of the phosphine ($\delta = 23.3$ ppm) and phosphite ($\delta = 127.3$ ppm) resonances (Figure 2). Also evident is a new resonance appearing at $\delta = 139.8$ ppm in the

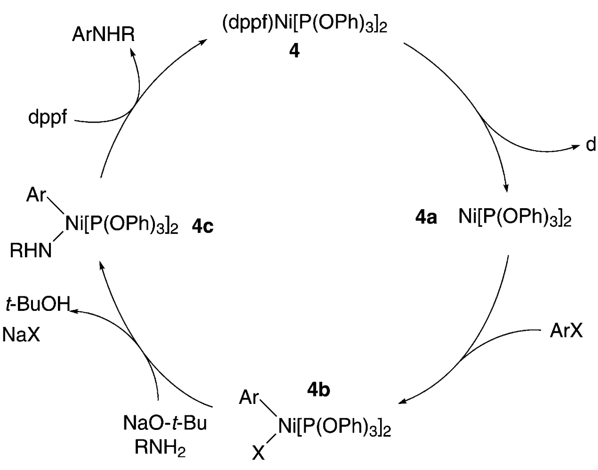


Figure 2. Proposed catalytic cycle.

phosphite region of the spectra, however, not corresponding to free phosphite ($\delta = 127.9$ ppm). An increase in the intensity of the free dppf phosphine resonance $\delta = -16.4$ ppm is also clear. Both these factors suggest that a bis-phosphite nickel complex **4a** is possibly formed in the early stages of the reaction. Following other Ni(0)/Ni(II) catalytic cycles proposed for nickel catalyzed C–N coupling reactions,[47,48] an oxidative addition to Ar(X)Ni[P(OPh)$_3$]$_2$ **4b** and base-promoted amination to Ar(RHN)Ni[P(OPh)$_3$]$_2$ **4c** is estimated. The final, and possibly slow, reductive elimination is suggested to be assisted through the coordination of dppf. The role of the additional dppf, however, cannot be confirmed at this stage. The GC analysis of the reaction mixture (see the Supporting Information) highlights an impressive conversion (4% → 56%) for this reaction between the sampling at the 15 and 30 min time periods. We are currently pursuing a more detailed kinetic study of this reaction to determine; the rate-limiting step of the reaction, the roles of dppf and the solvent.

In conclusion, we have identified nickel phosphites that can serve as more stable replacements for Ni(COD)$_2$. Additionally, the nickel phosphite/phosphine complex **4** serves as an excellent catalyst for C–N amination reactions of various aryl chlorides and anilines or amines. Interestingly, the addition of a second phosphine (dppf or *rac*-BINAP) assists in the coupling process. However, further studies are required to identify and confirm the structures of intermediates from the proposed catalytic cycle for this coupling process.[23,47,49]

Experimental Section

[1,1′-Bis(diphenylphosphino)ferrocene]bis(triphenyl phosphite)nickel(0) (4)

Ni[P(OPh)$_3$]$_4$ (10.0 g, 7.67 mmol, 1.00 equiv.) and dppf (8.50 g, 15.3 mmol, 2.00 equiv.) were placed in a flame-dried Schlenk flask and dried under high vacuum for 10 min. Toluene (250 mL) was added *via* cannula transfer and the resulting orange solution was heated to reflux for 2 h. The solution was concentrated to *ca.* 100 mL under vacuum (cold trap) and *n*-hexane (200 mL) was added *via* cannula transfer. The ensuing yellow precipitate was filtered under an argon atmosphere, washed with *n*-hexane (3 × 20 mL), and dried under high vacuum to give (dppf)Ni[P(OPh)$_3$]$_2$ (**4**) as a yellow powder; yield: 8.62 g (6.99 mmol, 91%); m.p. = 158–160 °C (decomposition). ^{1}H NMR (600 MHz, C_6D_6): $\delta =$ 7.59 (t, $J = 8.1$ Hz, 8H), 7.09 (d, $J = 7.2$ Hz, 3H), 7.05 (t, $J = 7.1$ Hz, 8H), 7.00–6.89 (m, 24H), 6.80–6.75 (m, 7H), 4.26 (s, 4H, Cp), 3.93 (s, 4H, Cp); ^{13}C NMR (150 MHz, C_6D_6): $\delta =$ 153.8, 152.4, 151.2 (d, $J = 7.1$ Hz), 141.3 (d, $J = 29.1$ Hz), 134.8 (d, $J = 14.4$ Hz), 131.7, 130.03 (d, $J = 2.3$ Hz), 129.2, 128.4, 125.6, 124.5, 123.2, 122.2, 121.2, 120.6 (d, $J = 5.0$ Hz), 74.8 (d, $J = 9.4$ Hz, Cp), 73.9 (d, $J = 33.1$ Hz, Cp), 71.2 (d, $J = 3.7$ Hz, Cp); ^{31}P NMR (243 MHz, C_6D_6): $\delta = 127.3$ (t, $J = 28.8$ Hz), 23.3 (t, $J = 28.8$ Hz); IR (ATR) $\nu = 3056$, 1590, 1486, 1435, 1188, 1161, 1093, 1025, 958, 871, 745, 722, 686, 566, 524 cm^{-1}.

Crystals suitable for X-ray diffraction were obtained by placing a solution of the complex in dry and degassed toluene/*n*-hexane (1:1) in the freezer for one day. Please see supporting information for more details. CCDC 983669 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for C–N Cross-Coupling Reactions

A flame-dried Schlenk tube was loaded sequentially with NaO-*t*-Bu (201 mg, 2.10 mmol, 1.40 equiv.), (dppf)Ni-[(OPh)$_3$]$_2$ (**4**) (93 mg, 75 μmol, 5 mol%), dppf (42 mg, 75 μmol, 5 mol%), the corresponding amine (1.80 mmol, 1.20 equiv.), and aryl chloride (1.50 mmol, 1.00 equiv.). The mixture was dissolved in toluene (6 mL), placed into a preheated oil bath at 100 °C and stirred for 18 h. Upon cooling, the reaction mixture was fused onto silica and purified *via* flash column chromatography (hexanes/EtOAc or DCM/MeOH) to give the desired product.

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