[NiCl₂(dppp)]-Catalyzed Cross-Coupling of Aryl Halides with Dialkyl Phosphite, Diphenylphosphine Oxide, and Diphenylphosphine**

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Abstract: We present a general approach to C–P bond formation through the cross-coupling of aryl halides with a dialkyl phosphite, diphenylphosphine oxide, and diphenylphosphane by using [NiCl₂(dppp)] as catalyst (dppp=1,3-bis(diphenylphosphino)propane). This catalyst system displays a broad applicability that is capable of catalyzing the cross-coupling of aryl bromides, particularly a range of unreactive aryl chlorides, with various types of phosphorus substrates, such as a dialkyl phosphite, diphenylphosphine oxide, and diphenylphosphane. Consequently, the syn-

thesis of valuable phosphonates, phosphine oxides, and phosphanes can be achieved with one catalyst system. Moreover, the reaction proceeds not only at a much lower temperature (100–120 °C) relative to the classic Arbuzov reaction (ca. 160–220 °C), but also without the need of external reductants and supporting ligands. In ad-

Keywords: aryl halides • C–P bond formation • homogeneous catalysis • nickel • phosphine oxide • phosphites dition, owing to the relatively mild reaction conditions, a range of labile groups, such as ether, ester, ketone, and cyano groups, are tolerated. Finally, a brief mechanistic study revealed that by using [NiCl₂(dppp)] as a catalyst, the Ni^{II} center could be readily reduced in situ to Ni⁰ by the phosphorus substrates due to the influence of the dppp ligand, thereby facilitating the oxidative addition of aryl halides to a Ni⁰ center. This step is the key to bringing the reaction into the catalytic cycle.

boranes.^[10] In addition, a few protocols based on Cu catalysts have also been reported.^[11] However, a general catalyst system that is capable of catalyzing the cross-coupling of

various types of phosphorus substrate is absent. Moreover,

highly reactive aryl iodides or triflates combined with a long

reaction time and/or high temperature was essentially re-

quired in most cases. The coupling of readily available aryl

As another premier method for C_{sp2}-P bond formation,

the Ni-catalyzed reaction of aryl halides with trialkyl phos-

phites $(P(OR)_3)$, namely, the Tavs or Arbuzov reaction,^[12] is

also promisingly attributed to the use of ligand-free NiX₂

(X = Cl and Br) compounds as catalysts and under base-free conditions.^[13] However, this protocol has not been accepted as a common method owing to the high reaction temperature, which generally ranges from 160–220 °C. Moreover, the

reaction is often limited to trialkyl phosphites and other

phosphorus substrates, such as HP(O)(OR)₂, HP(O)R₂, and

HPR₂, have been rarely considered.^[14] A mechanistic

study^[12] revealed that the high thermal activation energy re-

quired in this reaction arises mainly from the reduction of

 Ni^{II} to Ni^{0} (A₁) and the oxidative addition of aryl halides to

To overcome these problems, very recently, Zhao and co-

workers^[15] disclosed a useful method for the coupling of

ArX (X=I, Br) and diphenylphosphine oxide in aqueous

media at 70 °C. This method represents a great advance in

Ni-catalyzed C-P bond formation. However, a combination

of 2.0 equivalents of Zn powder as external reductant and

 A_1 to form the Ni^{II} species (A_2 ; Scheme 1).

chlorides has been largely unexplored.

Introduction

Despite the great advance in transition-metal-catalyzed C_{sp^2} -X (X=C, N, O, S, and so forth) bond formation over the past decades, relatively limited protocols for C–P coupling are available. This fact belies the importance of phosphorus compounds, such as phosphonates, phosphine oxides, and phosphanes, in materials science,^[1] biochemistry,^[2] and catalytic chemistry.^[3] Since the pioneering work of Hirao et al.,^[4] the Pd-catalyzed cross-coupling reactions of aryl halides with various phosphorus compounds have been frequently studied,^[5] including H-phosphine oxides,^[6] H-phosphites,^[7] H-phosphanes,^[8] silylphosphanes,^[9] and phosphane-

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- [**] dppp=1,3-bis(diphenylphosphino)propane.

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Scheme 1. Reaction mechanism of a Ni-catalyzed C–P bond-formation reaction between aryl halides and trialkyl phosphites.

20 mol% of 2,2'-bipyridine (bpy) as an external ligand were required for effective cross-coupling.

On the basis of our well-established experiences in Ni-catalyzed C-C cross-coupling^[16] and a careful analysis of the Tavs reaction mechanism,^[12] we have become interested in developing an active Ni catalyst system for a general and mild C-P bond formation under conditions that are external-reductant and ligand free. Such a procedure would be more appealing in terms of the philosophy of efficient synthesis referred to as atom economic and green.^[17] Herein, we disclose that the [NiCl₂(dppp)] complex is a highly active catalyst that allows C-P coupling to proceed smoothly without the need of external reductants and external supporting ligands at a significantly lower temperature relative to the conventional Arbuzov reaction. Most significantly, the catalyst exhibits a broad applicability not only to aryl halides but also to various types of phosphorus substrate, such as $HP(O)(OR)_2$, $HP(O)R_2$, and HPR_2 .

Results and Discussion

To develop a Ni-based catalyst that is not only universally applicable but also highly active, we designed a ligand-based strategy. Because numerous reports have demonstrated that the redox property of a transition-metal ion is affected profoundly by the nature of the ligated ligands,^[18] we assumed that the reduction of Ni^{II} to Ni⁰ should also occur easily if a Ni^{II} complex coordinates with an appropriate ligand, thereby making the oxidative addition of an aryl halide to a Ni⁰ center proceed under mild conditions. Consequently, the thermal activation energy of the whole catalytic cycle would be lowered.

With this assumption in mind, an extensive survey of the reaction conditions was carried out (Table 1). Initially, the catalytic efficiency of free [NiCl₂ and various nickel complexes was evaluated (Table 1, entries 1–7). The results showed that among several nickel complexes [NiCl₂(dppp)] is

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a potential catalyst, thus affording the desired product **3a** in 75% yield at a considerably lower temperature of 100°C (Table 1, entry 5). In addition, a base is also indispensable in this transformation because it may act to deprotonate the H-phosphonate diester.^[19] K₃PO₄ was optimal, as seen from the results (Table 1, entries 5 and 8–14). A brief examination of solvents suggested that dioxane was a better option (Table 1, entries 5 versus 15–18).

With the optimized catalyst, base, and solvent, we further inspected the effect of external ligands, such as bpy, dppf, PCy_3 , and 2-(di-*tert*-butylphosphino)biphenyl on the transformation. Unfortunately, a markedly lowered yield of **3a** was observed in the presence of various external ligands (Table 1, entries 19–22). These results further demonstrated

Table 1. Optimization of the reaction conditions.[a]



[a] Reaction conditions: 1-bromonaphthalene (**1a**; 1.0 mmol), dimethyl phosphite (**2**), [NiCl₂(dppp)], K₃PO₄, solvent (4 mL), 100 °C, 6–12 h. [b] Yield of the isolated product. [c] No reaction (n.r.). [d] The catalyst was pre-prepared in situ by stirring NiCl₂ and AsPh₃ or dppf for 3 h in dioxane at 100 °C and the other reagents were charged. [e] No base was used. [f] Stirred at 80 °C. [g] 2,2'-Bipyridine (5 mol %) was used as an external ligand. [h] Dppf (5 mol %) was used as an external ligand. [j] PCy₃ (10 mol %) was used as an external ligand. DIPEA = diisopropylethylamine, dppe = 1,2-bis(diphenyl-phosphino)ethane, dppf = 1,1'-bis(diphenyl-phosphino)ferrocene, PCy₃ = tricyclohexyl-phosphine.

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our assumption that ligands play a crucial rule in the coupling. Finally, the loading amount of $[NiCl_2(dppp)]$ and the amount of K_3PO_4 and dimethyl phosphite were optimized (Table 1, entries 23–27). Extensive surveys of various reaction parameters led to the following optimized conditions: dimethyl phosphite (2.0 equiv), $[NiCl_2(dppp)]$ catalyst (10 mol%), and K_3PO_4 (2.0 equiv) in dioxane at 100°C. Under these conditions, aryl phosphonate **3a** could be obtained in 91% yield (Table 1, entry 26).

Having established the optimized conditions, we examined the generality of the methodology by varying the structures of the aryl halides. Unsubstituted naphthyl bromides reacted smoothly with phosphite 2 to afford the coupled products 3a and 3b in excellent yields (Table 2). In addition,

Table 2. Cross-coupling of dimethyl phosphite with various aryl halides.^[a]



[a] Reaction conditions: aryl halide (0.5 mmol), dimethyl phosphite (**2**; 1.0 mmol), [NiCl₂(dppp)] (10 mol%), K₃PO₄ (1.0 mmol, 2.0 equiv), dioxane (2 mL), 100 °C, 6-24 h; the yield of the isolated product is given. [b] Reaction was carried out at 120 °C. [c] The yield was determined by ¹H NMR spectroscopic analysis due to the contamination of a small amount of inseparable deacetylated product.

naphthyl analogues modified either by a strong electron-rich OMe group or an electron-deficient ester group also underwent smooth coupling to afford **3c** and **3d**, respectively. Moreover, a range of the nonfused aromatics (i.e., less electron-deficient systems) are also viable substrates. For instance, bromobenzene substituted with electron-withdrawing acetyl and cyano groups at the *para-* and *meta-*positions were coupled with dimethyl phosphite in high yields to give **3e** and **3f**. Equally interestingly, heteroaromatic bromides are also compatible with the reaction conditions, as exemplified by the coupling of 3-bromoquinoline (**3j**) and *N*-acetyl indole (**3k**). It should be noted that although good coupling efficiencies were generally observed for an array of aryl bromides, the poor yields for **3h** and **3i** suggest that sterically hindered and electronically enriched phenyl substrates suppress the reaction. Based on the reaction mechanism,^[12] these factors may decrease the rate of oxidative addition of aryl halides to the Ni^0 center and/or the reductive elimination.

Some more results of interest: the reaction is tolerant of a range of aryl chlorides with structural features that are similar to aryl bromides, including delocalized naphthyl (3a,b), less-delocalized phenyl (3e,g), and heteroaromatic (3l) chlorides, although a somewhat elevated temperature is required (120 °C). These results are of particular interest because aryl chlorides are widely available and much cheaper than aryl bromides and iodides. However, a general procedure for the coupling of this class of substrate has been

> largely unexplored in transition-metal-catalyzed C– P bond formation owing to the notoriously unreactive nature of these compounds.^[20] It is also worth noting that due to the significantly lowered reaction temperature, a range of functional groups on the aryl-ring periphery, such as ether, ester, ketone, and cyano groups, is tolerated.

> Having examined the scope and limitations of the methodology for the cross-coupling of aryl halides with phosphite compounds, we shifted our attention to the coupling reactions with phosphine oxides as the phosphorus source. Accordingly, the reaction of 1-bromonaphthalene 1 and diphenylphosphine oxide (4) was investigated (Table 3). The results showed that 1 could be coupled far more efficiently with diphenylphosphine oxide than with dimethyl phosphite (2). Complete conversion and an excellent yield of 5a were obtained under the otherwise identical conditions used to couple phosphite 2, except that the catalyst loading and molar ratio of phosphine oxide 4 were decreased to 5 mol% and 1.5 equivalents, respectively. Furthermore, these conditions also exhibit a broad compatibility with a rich range of aryl bromides and unreactive chloride derivatives, including delocalized naphthyl substrates (5a-d), less-delocalized phenyl compounds (5e-i), and heteroarenes (5k-o), except that a deactivated substrate (5j) is less reactive. More to the

point, relative to the outcome with dimethyl phosphite (**3h**, Table 2), the sterically hindered *ortho*-cyano-substituted aryl bromide can be coupled smoothly with diphenylphosphine oxide to give **5i** in 94% yield. Finally, the reaction is also tolerant of various functional groups.

Next, we investigated the reaction of aryl halides with secondary phosphine **6**. A wide array of aryl bromides including naphthyl (Table 4, entries 1–8), phenyl (Table 4, entries 9–12), heteroaromatic (Table 4, entries 13–16), and a compound with a sterically encumbered structural motifs (entry 12, Table 4) underwent smooth coupling with diphenylphosphine **6** (1.2 equiv) in the presence of 5 mol% [NiCl₂(dppp)]. Although high-to-excellent overall yields were observed for various aryl halides, the coupling reaction formed a mixture of phosphine oxides **5** and phosphines **7**. Table 3. Cross-coupling of various aryl halides with diphenylphosphine oxide.^[a]



[a] Reaction conditions: aryl halide (0.5 mmol), diphenylphosphine oxide (4; 0.75 mmol), $[NiCl_2(dppp)]$ (5 mol%), K_3PO_4 (1.0 mmol, 2.0 equiv), dioxane (4 mL), 100°C, 12–24 h; the yield of the isolated product is given. [b] The reaction was carried out at 120°C.

Despite this drawback, the method still has some interesting points because both phosphines **7** and phosphine oxides **5** are valuable compounds. Furthermore, they can be transformed with respect to each other by means of oxidation or reduction reactions. In addition, phosphines and phosphine oxides can be easily separated by column chromatography.

More importantly, the observation of phosphine oxide 5 has further implications. It may provide an alternative pathway for the synthesis of phosphine oxides from H-phosphines. To this end, we inspected the reasons for the formation of phosphine oxides 5. Several control experiments were carried out, the results showed that external addition of 1 or 2% H₂O (v/v) to the reaction mixture of 2-bromonaphthalene and 6 resulted in a negligible change in the ratio of 7b/5b (Table 4, entry 2 versus entries 3 and 4). These observations ruled out the influence of a trace amount of water on the reaction. In addition, 5b was not observed by stirring a solution of triarylphosphine 7b in an oxygen atmosphere overnight, thus suggesting that 5b was not formed from the oxidation of 7b. However, when the reaction was carried out in an oxygen atmosphere diluted with nitrogen, phosphine oxide 5b was obtained as the major product, although the total yield was somewhat diminished (Table 4, entry 5). Thus, a summary of the results on the control experiments suggested that the formation of phosphine oxides 5 is due most possibly to the trace amount of

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oxygen involved in the reaction system, although all the reagents and solvent were degassed prior to use. Namely, the oxidation of phosphine **6** by the trace amount of oxygen generates the corresponding secondary phosphine oxide **4**, and the product **4** is coupled with aryl halides to produce the triarylphosphine oxide **5**.

To demonstrate the utility of this result, the direct synthesis of triarylphosphine oxide **5b** from phosphine **6** was explored. After examining different procedures, phosphine oxide **5b** could be obtained in 87% yield as a single product when the reaction was carried out by a prior oxidation of phosphine **6** in an oxygen atmosphere at room temperature, followed by recharging of 2-bromonaphthalene and [NiCl₂(dppp)] to the reaction vessel in situ and heating the reaction mixture at 100°C (Table 4, entry 6). The yield is comparable to the coupling of 2-bromonaphthalene and H-diphenylphosphine oxide (**4**; 95% yield; **5b** in Table 3).

On the other hand, to suppress the formation of phosphine oxides, we investigated the coupling of the H-phosphine–borane complex $[(HPPh_2)BH_3]$ instead of HPPh₂. Unfortunately, the phosphine–borane complex displayed a markedly lower reactivity, with only small amount of coupled products of triarylphosphine and triarylphosphine oxide observed under the reaction conditions. Control experiments revealed that by heating at 100°C, HPPh₂BH₃ decomposes slowly to Ph₂PH, which was oxidized partially to Ph₂P(O)H. Consequently,

 Ph_2PH and $Ph_2P(O)H$ were coupled with any halides to form triarylphosphines and triarylphosphine oxides, respectively, in the reaction mixture.

Finally, to confirm whether the general and mild C-P cross-coupling is really promoted by the ligand-based strategy (see above), three control experiments were carried out. When a mixture of 1-bromonaphthalene, K₃PO₄, and [NiCl₂-(dppp)] was heated in dioxane at 100°C for one hour, no observable change resulted because the [NiCl₂(dppp)] particles remained insoluble. In contrast, when the aryl halide was replaced by dimethyl phosphite or diphenylphosphine oxide, a slight- or deep-yellow homogeneous solution, respectively, was formed rapidly within several minutes. These observations are in good agreement with the previous experimental description,^[12] thus indicating that a Ni⁰ complex was formed in the system. The results were further confirmed by X-ray photoelectron spectroscopic (XPS) analysis; namely, the nickel $2p^{3/2}$ binding energies for the two nickel species treated by dimethyl phosphite 2 and diphenylphosphine oxide 4 were 852.4 and 853.1 eV, respectively, which are almost the same as that for Ni⁰ powder (i.e., 852.8 eV) and some other Ni⁰ complexes.^[21] In contrast, the nickel 2p^{3/} ² binding energy for the divalent [NiCl₂(dppp)] complex was 855.1 eV. Thus, the combination of the control experiments and XPS analysis clearly demonstrated that by appropriate design of the ligands the reduction of the metal center from

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Table 4. Cross-coupling of various aryl halides with diphenylphosphine.^[a]

	Ar-Br + H-P-Ph	[NiCl ₂ (dppp)] (5 %) K_3PO_4 (2.0 equiv) $\Lambda_r = P = Pb + \Lambda_r = P = Pb$			
	Ph	dioxane (2	mL) Ph Ph		
Entry	Product 7	Yield of 7 [%] ^[b]	Product 5	Yield of 5 [%] ^[b]	Yield of 5+7 [%]
1		70	O PP-Ph Ph	24	94
2 3 4 5 6	P-Ph Ph 7b	58 54 58 8 0	O Ph 5b	39 41 39 56 87	97 ^[c] 95 ^[d] 97 ^[e] 64 ^[f] 87 ^[g]
7	MeO 7c	42	MeO 5c	51	93
8	MeO ₂ C 7d	49	MeO ₂ C 5d	47	96
9	Me 7e P-Ph Ph	25	Me O O Se	63	88
10	of Ph Ph 7f	30	of P-Ph	47	77
11	MeO ₂ C- / 7g	47	MeO ₂ C-C-C-P-Ph Ph 5g	46	93
12	P ^{-Ph} _{Ph} CN 7h	72	P-Ph Ph CN 5i	8	80
13	Ph Ph 7i	51	P-Ph Ph 5k	48	99
14	P-Ph Ph 7j	68		12	80
15	P - Ph Ph N 7k	42	P-Ph Ph N 5m	48	90
16	N Me 71	31	Me 5n	54	85

[a] Reaction conditions: aryl halide (0.5 mmol), diphenylphosphine **6** (0.6 mmol), [NiCl₂(dppp)] (5 mol%), K₃PO₄ (1.0 mmol, 2.0 equiv), dioxane (2 mL), 100°C, 10–18 h. [b] Yield of the isolated product. [c] Average yield of three trials in anhydrous dioxane. [d] Average yield of two trials by adding 1% H₂O (v/v). [e] Average yield of three trials by adding 2% H₂O (v/v). [f] Average yields of two runs. The reaction was carried out in an oxygen atmosphere diluted with nitrogen (O₂/N₂=1:4 (v/v)). [g] Phosphine **6** was stirred in an oxygen atmosphere diluted with nitrogen (O₂/N₂=1:2 (v/v)) for 3 h at room temperature. The aryl halide and [NiCl₂(dppp)] were then added to the reaction mixture, which was stirred at 100°C.

Ni^{II} to Ni⁰ by various phosphorus substrates in situ and the subsequent Ni⁰-catalyzed C-P bond formation proceeded at a significantly lower temperature without the need of external reductants and supporting ligands. Finally, it should be mentioned that although the important role of the dppp ligand in affecting the general and relatively mild C-P coupling reaction has been demonstrated, phosphites, phosphine oxides, and phosphines may also serve as coligands to promote this transformation because these phosphorus compounds were effective ligands in the Suzuki-Miyaura crosscoupling,^[22] C-P bond addition,^[23] and other reactions.^[24]

Conclusion

By utilizing a ligand-based strategy, we have achieved a Ni⁰-catalyzed cross-coupling of aryl halides with various phosphorus substrates under relatively mild reaction conditions in the absence of external reductants and supporting ligands. As one of its notable features, this method allows aryl bromides and, particularly, less-reactive aryl chlorides to be coupled efficiently. In addition, a range of functional groups, such as ether, ester, ketone, and cyano groups, are also tolerated, which is attributed to the mild conditions. Moreover, the method exhibits good compatibility with various types of phosphorus substrate, such as a H-phosphite, H-phosphine oxide, and H-phosphine. To the best of our knowledge, a catalyst system that not only enables C-P bond formation under mild conditions but also exhibits such a broad applicability both to aryl halides and phosphorus sources that has been rarely disclosed. Finally, the $[NiCl_2(dppp)]$ catalyst is cheap, readily available, and markedly air and moisture stable, thus facilitating operation on the benchtop. Owing to these advantages, we believe the method presented herein should find a broad application in C–P bond formation.

Experimental Section

General methods: All the reactions were carried out under N₂. The dioxane solvent was dried over molecular sieves (4 Å) or distilled according to the standard method. Anhydrous NiCl₂ and the ligands were purchased from J&K Chemical Ltd and Alfa Aesar, respectively. Unless otherwise noted, the ¹H and ¹³C NMR spectra were recorded at 400 (or 600) and 100 (or 150) MHz, respectively, in CDCl₃ with trimethylsilane (TMS) as an internal standard. All the chemical shifts were given in ppm. All coupling constants *J* are reported in Hertz (Hz).

General procedure for Ni-catalyzed cross-coupling reactions of aryl halides with phosphorus substrates (with the coupling of aryl halides with dimethyl phosphite as a representative): An aryl halide (0.5 mmol, 1.0 equiv), [NiCl₂(dppp)] (10 mol%), and anhydrous K₃PO₄ (1.0 mmol, 2.0 equiv) were added to a 25 mL Schlenk tube equipped with a magnetic bar. The tube was evacuated (3×10 min) under vacuum and backfilled with N2. Dimethyl phosphite and dried dioxane (2.0 mL) were injected through a syringe, and the reaction mixture was stirred at 100°C (120°C for aryl chlorides) until the aryl halide had disappeared, as monitored by TLC analysis. The reaction mixture was poured into water (30 mL) and extracted with CH2Cl2 (3×20 mL). The combined organic layers were dried over anhydrous Na2SO4, filtered, and concentrated to dryness. The crude material was purified by flash chromatography on silica gel with hexane/acetone (or hexane/ethyl acetate) as the eluent to obtain the desired cross-coupled products. See the Supporting Information for detailed experimental procedures, characterization data, and the 1H and 13C NMR spectra of the coupled products.

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