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C–P Bond-Forming Reactions via C–O/P–H Cross Coupling Catalyzed by Nickel

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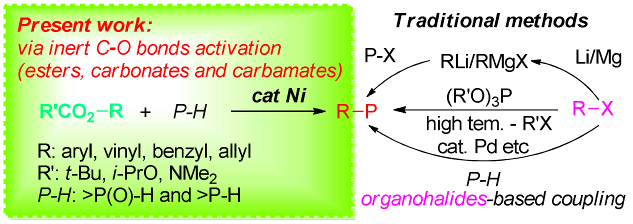
Supporting Information Placeholder

ABSTRACT: The first Ni-catalyzed C–O/P–H cross coupling producing organophosphorus compounds is disclosed. This method features a wide generality regarding to both C–O and P–H compounds, i.e., as to C–O compounds, the readily available alcohol derivatives of aryl, alkenyl, benzyl and allyl are applicable, and as to P-H compounds, both >P(V)(O)H compounds (secondary phosphine oxide, H-phosphinate and H-phosphonate) and hydrogen phosphines >P(III)H all can be used as the substrates. Thus, a variety of the valuable sp^2C–P and sp^3C–P compounds are readily obtained in good to excellent yields by this new strategy.

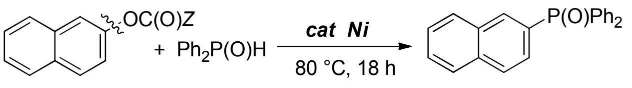
Organophosphorous compounds are useful chemicals in organic synthesis, catalysis, medicinal chemistry, materials and coordination chemistry.[1] The development of a cleaner and more efficient method for their preparation to replace the old ones is of current concern.[2–7] Nowadays, organophosphorus compounds are most prepared, both in the laboratory and industry, via the transformation of organohalides (Scheme 1).[2-6] Thus, the orthodoxy nucleophilic substitutions of the toxic phosphorus halides with organolithiums or Grignard reagents produce the corresponding organophosphorus compounds. The reaction of an excess amount of a halide with a phosphite (Michaelis-Arbusov reaction) is also extensively used for the preparation of an organophosphoryl compound, despite the harsh condition, low efficiency and substrate limitations.[4] In 1980s, Hirao et al disclosed a palladium-catalyzed coupling of ArX (X = Br, I) with P(O)–H compounds under mild conditions. This reaction is now widely used as a reliable method for the construction of C–P bonds because of its high efficiency and good tolerance to functionallities.[5,6]

Scheme 1. C–P bond formations



Herein, we disclose an efficient inert C–O/P–H cross coupling to produce organophosphorus compounds in high yields under mild conditions using a cheap nickel catalyst (Scheme 1). Alcohols and their derivatives are abundant raw chemical materials. Compared to organohalides, they are environmentally friendly and cost-saving. However, to our knowledge, the synthesis of an organophosphorus compound via such a transformation of an inert C–O bond has never been realized.[7–11]

Table 1. Ni-catalyzed coupling of 2-naphthyl pivalate 1a and analogues with diphenylphosphine oxide 2a.[a]



1a, Z = *t*-Bu; **1a'**, Z = *i*-PrO
1a'', Z = Me_2N

3a

entry	ligand	base	solvent	yield(%)(**3a**/**3a'**)[b]
1	20 mol% PPh_3	K_2CO_3	dioxane	none
2	20 mol% PCy_3	K_2CO_3	dioxane	none
3	10 mol% dppe	K_2CO_3	dioxane	none
4	10 mol% dppp	K_2CO_3	dioxane	none
5	10 mol% dppb	K_2CO_3	dioxane	none
6	10 mol% dppf	K_2CO_3	dioxane	none
7	10 mol% dcype	K_2CO_3	dioxane	91(98/2)
8	5 mol% dcype	K_2CO_3	dioxane	66(90/10)
9	10 mol% dcype	Et_3N	dioxane	24(85/15)
10	10 mol% dcype	Na_2CO_3	dioxane	37(75/25)
11	10 mol% dcype	Cs_2CO_3	dioxane	33(60/40)
12	10 mol% dcype	*t*-BuONa	dioxane	<5(4/96)
13[c]	10 mol% dcype	K_2CO_3	dioxane	69(98/2)
14[d]	10 mol% dcype	K_2CO_3	dioxane	95(98/2)
15[e]	10 mol% dcype	K_2CO_3	dioxane	none
16	10 mol% dcype	K_2CO_3	THF	91(93/7)
17	10 mol% dcype	K_2CO_3	toluene	70(91/9)
18	10 mol% dcype	K_2CO_3	DMF	20(46/54)
19[d,f]	10 mol% dcype	K_2CO_3	dioxane	95(98/2)
20[d,g]	10 mol% dcype	K_2CO_3	dioxane	85(98/2)

[a]Reaction conditions: a mixture of **1** (0.1 mmol), $Ph_2P(O)H$ (0.1 mmol), 10 mol% $Ni(COD)_2$ (0.01 mmol), a phosphine ligand

(Ni/P = 1:2) and a base (0.1 mmol) in a solvent (0.5 mL) was heated at 80 °C for 18 h. [b]**3a'**: (2-naththyl)diphenylphosphine. GC yield using tredecane as an internal standard. [c]60 °C. [d]100 °C. [e]no addition of Ni(COD)$_2$. [f]**1a'** was used. [g]**1a''** was used.

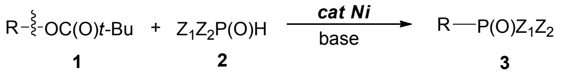
Thus, at 80 °C, a mixture of 2-naphthyl pivalate **1a** and diphenylphosphine oxide **2a** dissolved in dioxane was allowed to react in the presence of potassium carbonate, Ni(COD)$_2$ and a phosphine ligand (Table 1). The use of a proper phosphine ligand is crucial for this reaction. No reaction took place with PPh$_3$, PCy$_3$, dppe (1,2-bis(diphenylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane), dppb (1,4-bis(diphenylphosphino)butane), and dppf (1,1'-bis(diphenylphosphino)ferrocence). When dcype (1,2-bis(dicyclohexylphosphino)ethane) was used as the ligand, the coupling reaction of **1a** with **2a** proceeded efficiently to produce the coupling product **3a** and its reduced form **3a'**[12] in 91% combined yield (entry 7). The yield of the coupling products decreased to 66% when 5% of dcype was used (entry 8). The choice of a proper base was also crucial to this coupling reaction. The yields were low when Et$_3$N, Na$_2$CO$_3$ and Cs$_2$CO$_3$ were used (entries 9–11). In addition, the ratio of the reduced product **3a'** increased. Under similar conditions, sodium *tert*-butoxide only gave a trace amount of the products (entry 12). The reaction also proceeded at a lower temperature (60 °C), although the yield decreased to 69% (entry 13). The nickel catalyst is essential, because no product was obtained in the absence of the catalyst (entry 15). As to the solvent, this coupling reaction also proceeded efficiently in THF (entry 16) and toluene (entry 17), but poorly in DMF (entry 18). In addition to the ester **1a**, a carbonate **1a'** and a carbamate **1a''** could also be used as the substrates to produce the coupling product **3a** in 95% and 85 % yields, respectively (entries 19 and 20).[13]

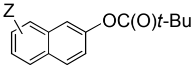
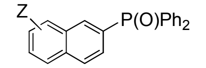
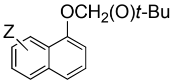
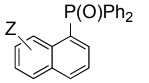
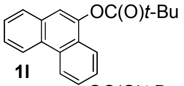
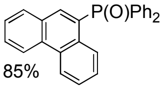
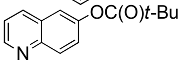
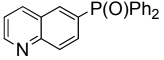
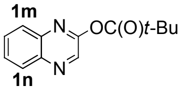
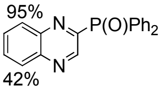
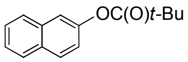
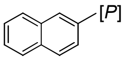
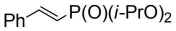
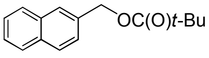
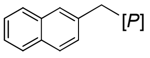
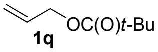
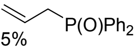
This Ni-catalyzed C–O/P–H cross coupling is a rather general reaction for the construction of P–C bonds. As shown in Table 2, a variety of esters **1** could readily couple with hydrogen phosphoryl compounds **2** under mild reaction conditions to produce the corresponding phosphoryl compounds **3** in high yields. High yields of **3** were obtained with both electron-rich and electron-deficient naphthyl pivalates (entries 2–5). Thus, derivatives of naphthyl pivalates bearing methoxy group at 7, 6, and 4 positions all gave the corresponding coupling products in good yields (entries 2, 3, 9). The substrate with an electron-withdrawing cyano group (entry 5) also produced the product **3e** in 88% yield. Functional groups such as an amide (entry 4) and an aldehyde (entry 6) were tolerable under the present conditions. Interestingly, double cross couplings took place with esters bearing a chloro (entry 10) and a bromo (entry 7) group to produce bisphosphoryl compounds **3j** and **3g** in good yields. As exemplified by run 11, a bispivalate could be successfully diphosphorylated with Ph$_2$P(O)H in one pot, affording the corresponding product **3k** in 91% yield. Notably, a heterocyclic (entries 13 and 14) and polycyclic phosphine oxide (entry 12) were also efficiently prepared via a similar Ni-catalyzed C–O/P–H cross coupling.

It seems that all kinds of the >P(O)H hydrogen phosphoryl compounds are applicable to the current coupling reaction. Thus, in addition to the aromatic diphenylphosphine oxide, an aliphatic *n*-Bu$_2$P(O)H (entry 15) and *n*-BuPhP(O)H (entry 16) both produced the corresponding phosphine oxide in high yields under similar reaction conditions. Similarly, the Ni-catalyzed cross-couplings also took place efficiently with a hydrogen phosphinate (entry 17) and hydrogen phosphonates (entries 18 and 19).

The generality of this coupling reaction was further demonstrated by using other esters as substrates. An alkenyl phosphonate **3t** (entry 20) was prepared from the coupling with phenylethenylpivalate **1o**. In addition, benzylic (entries 21–25) and allylic esters (entry 26) could also be used as the substrates to produce the corresponding coupling products in good to excellent yields. It should be noted that such a catalytic carbon-heteroatom bond-forming via the activation of sp^3C–O bonds is rare till now.[10a]

Table 2. Nickel-catalyzed C-O/P(O)-H coupling.[a]

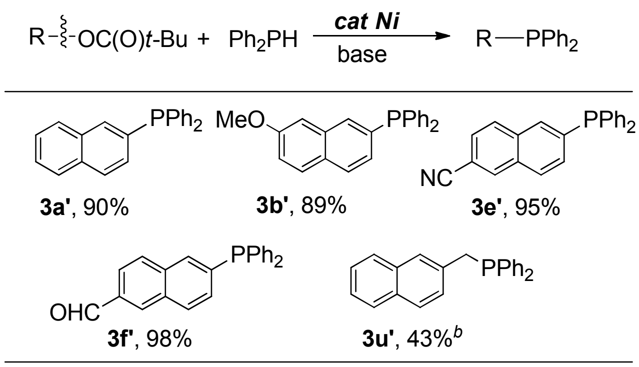


entry	R—OC(O)*t*-Bu	Z$_1$Z$_2$P(O)H	**3** (isolated yield)
		Ph$_2$P(O)H	
1	**1a**, Z = H		**3a**, Z = H, 90%
2[b]	**1b**, Z = 7-MeO		**3b**, Z = 7-MeO, 87%
3[b]	**1c**, Z = 6-MeO		**3c**, Z = 6-MeO, 83%
4[b]	**1d**, Z = 6-*t*-BuC(O)NH		**3d**, Z = 6-*t*-BuC(O)NH, 80%
5	**1e**, Z = 6-CN		**3e**, Z = 6-CN, 88%
6[b]	**1f**, Z = 6-CHO		**3f**, Z = 6-CHO, 51%
7[c]	**1g**, Z = 6-Br		**3g**, Z = 6-P(O)Ph$_2$, 90%
			
8	**1h**, Z = H		**3h**, Z = H, 91%
9[b]	**1i**, Z = 4-MeO		**3i**, Z = 4-MeO, 79%
10[c]	**1j**, Z = 4-Cl		**3j**, Z = 4-P(O)Ph$_2$, 95%
11[b]	**1k**, Z = 5-*t*-BuC(O)O		**3k**, Z = 5-P(O)Ph$_2$, 91%
12	 **1l**		 **3l**, 85%
13[b]	 **1m**		 **3m**, 95%
14[b]	 **1n**		 **3n**, 42%
			
15		*n*-Bu$_2$P(O)H	**3o**, [P] = *n*-Bu$_2$P(O), 98%
16		*n*-BuPhP(O)H	**3p**, [P] = *n*-BuPhP(O), 60%
17[b]		Ph(EtO)P(O)H	**3q**, [P] = Ph(EtO)P(O), 60%
18[b]		(EtO)$_2$P(O)H	**3r**, [P] = (EtO)$_2$P(O), 50%
19[b,d]		(*i*-PrO)$_2$P(O)H	**3s**, [P] = (*i*-PrO)$_2$P(O), 73%
20[b,d]	 **1o** (E/Z = 1:1)	(*i*-PrO)$_2$P(O)H	 **3t**, 43%
	 **1p**		
21[e]		Ph$_2$P(O)H	**3u**, [P] = Ph$_2$P(O), 88%
22[e]		*n*-Bu$_2$P(O)H	**3v**, [P] = *n*-Bu$_2$P(O), 72%
23[e]		*n*-BuPhP(O)H	**3w**, [P] = *n*-BuPhP(O), 95%
24[e]		Ph(EtO)P(O)H	**3x**, [P] = Ph(EtO)P(O), 62%
25[d,e]		(*i*-PrO)$_2$P(O)H	**3y**, [P] = (*i*-PrO)$_2$P(O), 70%
26	 **1q**	Ph$_2$P(O)H	 **3z**, 65%

[a]Reaction conditions: 1 mmol pivalate **1**, 1 mmol P(O)H compound **2**, 10 mol% Ni(COD)$_2$, 10 mol% dcype, 1 equiv K$_2$CO$_3$ and 5 mL dioxane were charged into a 10 mL sealed tube, and heated at 80 °C for 18 h. [b]100 °C. [c]120 °C, 20 mol% Ni(COD)$_2$, 20 mol% dcype, 2 equiv K$_2$CO$_3$ and 8 mL dioxane. [d]1.5 equiv P(O)–H was added. [e]1.5 equiv Cs$_2$CO$_3$, 8 mL dioxane, 100 °C.

Importantly, the substrates are not limited to the above mentioned >P(O)H compounds, even the highly coordinative secondary phosphine >P(III)H could be used as the P–H source in this nickel-catalyzed C–O/P–H cross coupling reaction to produce the valuable P(III) phosphines directly in high yields. As shown in Table 3, naphthyl pivalates with either an electron rich or an electron deficient group all were suitable for this cross coupling reaction. For instance, both methoxyl and cyano substituted naphthyl pivalates exhibited high reactivity with diphenyl phosphine to give the corresponding products in 89% and 95% yield, respectively. Notably, a substrate with a reactive aldehyde group also produced the expected corresponding phosphine in almost a quantitative yield (**3f'**). Benzylic pivalate **1p** also reacted with diphenyl phosphine to afford 43% yield of **3u'** under similar reaction conditions.

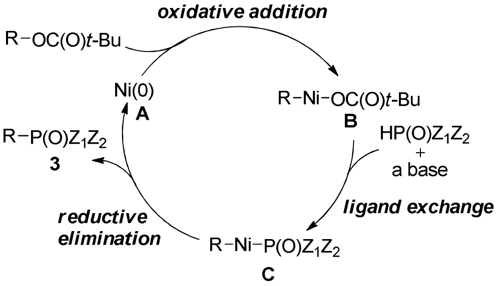
Table 3. Ni-catalyzed coupling of pivalates 1 with Ph_2PH.[a]



[a]Reaction conditions: 1 mmol pivalate, 1 mmol diphenylphosphine, 10 mol% $Ni(COD)_2$, 10 mol% dcype, 1.0 equiv K_2CO_3 and 5 mL dioxane were charged into a 10 mL sealed tube, and were heated at 120 °C for 18 h. The product was isolated as a phosphine oxide by oxidation with H_2O_2. [b]1.5 equiv Cs_2CO_3.

The mechanism is not fully understood. We propose that this Ni-catalyzed C–O/P–H cross coupling takes place via a catalytic cycle as shown in Scheme 2.[14] Ni(0) species, L–Ni(0)–dcype (**A**), generated from $Ni(COD)_2$ and dcype, first oxidatively adds to the C–O bond to produce **B**, which subsequently undergoes ligand exchange with a P–H compound by the aid of a base, giving an intermediate **C**. Finally, reductive elimination of **C** affords the coupling product **3** and regenerates the catalyst **A**.

Scheme 2. A proposed mechanism for the Ni-catalyzed C–O/P–H cross coupling.



In conclusion, we have developed an efficient Ni-catalyzed inert C–O/P–H cross coupling affording high yields of organophosphorus compounds under mild conditions. A variety of the readily available alcohol derivatives (aryl, alkenyl, benzyl and allyl) and PH compounds (both >P(O)H and >PH) can be used in this coupling reaction. We believe this is a new general protocol for the construction of the valuable C–P bonds from the readily available environmentally benign chemical sources. Works along this line, scope, limitation and mechanistic studies are currently under investigation.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, spectra data for all compounds, copies of ^1H, ^{13}C and ^{31}P NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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C–P Bond-Forming Reactions via C–O/P–H Cross Coupling Catalyzed by Nickel

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R = aryl, vinyl, benzyl, allyl

R' = *t*-Bu, *i*-PrO, NMe_2

P-H = >P(O)-H and >P-H