

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

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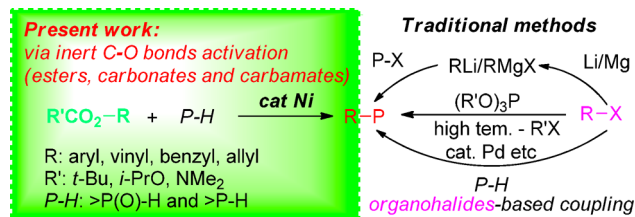
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**S** Supporting Information

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

Organophosphorus compounds are useful chemicals in organic synthesis, catalysis, medicinal chemistry, materials chemistry, and coordination chemistry.<sup>1</sup> The development of a cleaner and more efficient method for their preparation to replace the old ones is of current concern.<sup>2–7</sup> Nowadays, organophosphorus compounds are usually prepared, both in the laboratory and in industry, via the transformation of organohalides (Scheme 1).<sup>2–6</sup> Thus, orthodox nucleophilic

## Scheme 1. C–P Bond-Forming Reactions



substitutions of 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 (the Michaelis–Arbusov reaction) is also extensively used for the preparation of organophosphoryl compounds, despite the harsh conditions, low efficiency, and substrate limitations.<sup>4</sup> In the 1980s, Hirao and co-workers 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 functionalities.<sup>5,6</sup>

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 chemical raw materials. Compared with 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.<sup>7–11</sup>

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)<sub>2</sub>, and a phosphine ligand (Table 1). The use of a proper phosphine ligand was crucial for this reaction. No reaction took place with PPh<sub>3</sub>, PCy<sub>3</sub>, 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), or 1,1'-bis(diphenylphosphino)ferrocene (dppf). When 1,2-bis(dicyclohexylphosphino)ethane (dcype) 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'** in 91% combined yield (entry 7).<sup>12</sup> The yield of the coupling products decreased to 66% when 5 mol % dcype was used (entry 8). The choice of a proper base was also crucial to this coupling reaction. The yield was low when Et<sub>3</sub>N, Na<sub>2</sub>CO<sub>3</sub>, or Cs<sub>2</sub>CO<sub>3</sub> was used (entries 9–11). In addition, the relative amount 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 was essential, as no product was obtained in the absence of the catalyst (entry 15). In regard to the solvent, this coupling reaction also proceeded efficiently in tetrahydrofuran (THF) (entry 16) and toluene (entry 17) but poorly in *N,N*-dimethylformamide (DMF) (entry 18). In addition to ester **1a**, carbonate **1a'** and carbamate **1a''** could also be used as substrates to produce the coupling product **3a** in 95% and 85% yield, respectively (entries 19 and 20).<sup>13</sup>

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 com-

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Table 1. Ni-Catalyzed Coupling of 2-Naphthyl Pivalate (1a) and Analogues with Diphenylphosphine Oxide (2a)<sup>a</sup>

1a, Z = *t*-Bu; 1a', Z = *i*-PrO  
1a'', Z = Me<sub>2</sub>N

entry	ligand (mol %)	base	solvent	% yield (3a/3a') <sup>b</sup>
1	PPh <sub>3</sub> (20)	K <sub>2</sub> CO <sub>3</sub>	dioxane	none
2	PCy <sub>3</sub> (20)	K <sub>2</sub> CO <sub>3</sub>	dioxane	none
3	dppf (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	none
4	dppp (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	none
5	dppb (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	none
6	dppf (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	none
7	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	91 (98/2)
8	dcype (5)	K <sub>2</sub> CO <sub>3</sub>	dioxane	66 (90/10)
9	dcype (10)	Et <sub>3</sub> N	dioxane	24 (85/15)
10	dcype (10)	Na <sub>2</sub> CO <sub>3</sub>	dioxane	37 (75/25)
11	dcype (10)	Cs <sub>2</sub> CO <sub>3</sub>	dioxane	33 (60/40)
12	dcype (10)	<i>t</i> -BuONa	dioxane	<5 (4/96)
13 <sup>c</sup>	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	69 (98/2)
14 <sup>d</sup>	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	95 (98/2)
15 <sup>e</sup>	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	none
16	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	THF	91 (93/7)
17	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	toluene	70 (91/9)
18	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	DMF	20 (46/54)
19 <sup>d,f</sup>	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	95 (98/2)
20 <sup>d,g</sup>	dcype (10)	K <sub>2</sub> CO <sub>3</sub>	dioxane	85 (98/2)

<sup>a</sup>Reaction conditions: a mixture of **1** (0.1 mmol), Ph<sub>2</sub>P(O)H (0.1 mmol), 10 mol % Ni(COD)<sub>2</sub> (0.01 mmol), phosphine ligand (Ni/P = 1:2), and base (0.1 mmol) in the solvent (0.5 mL) was heated at 80 °C for 18 h. <sup>b</sup>3a' = (2-naphthyl)diphenylphosphine. GC yields using tridecane as an internal standard. <sup>c</sup>60 °C. <sup>d</sup>100 °C. <sup>e</sup>No addition of Ni(COD)<sub>2</sub>. <sup>f</sup>1a' was used. <sup>g</sup>1a'' was used.

pounds **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 pivalate bearing a methoxy group at the 7-, 6-, or 4-position all gave the corresponding coupling products in good yields (entries 2, 3, and 9). The substrate with an electron-withdrawing cyano group also gave the product **3e** in 88% yield (entry 5). Functional groups such as an amide (entry 4) and an aldehyde (entry 6) were tolerated under the present conditions. Interestingly, double cross-couplings took place with esters bearing a chloro group (entry 10) or a bromo group (entry 7) to produce bisphosphoryl compounds **3j** and **3g**, respectively, in good yields. As exemplified by run 11, a bispivalate could be successfully diphosphorylated with Ph<sub>2</sub>P(O)H in one pot, affording the corresponding product **3k** in 91% yield. Notably, heterocyclic (entries 13 and 14) and polycyclic (entry 12) phosphine oxides were also efficiently prepared via a similar Ni-catalyzed C–O/P–H cross-coupling.

It seems that all kinds of >P(O)H hydrogen phosphoryl compounds are applicable to the current coupling reaction. Thus, in addition to aromatic diphenylphosphine oxide, aliphatic *n*-Bu<sub>2</sub>P(O)H (Table 2, entry 15) and *n*-BuPhP(O)H (entry 16) both produced the corresponding phosphine oxides in high yields under similar reaction conditions. Similarly, the Ni-catalyzed cross-coupling also took place efficiently with a hydrogen phosphinate (entry 17) and hydrogen phosphonates (entries 18 and 19).

Table 2. Nickel-Catalyzed C–O/P(O)–H Cross-Coupling<sup>a</sup>

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

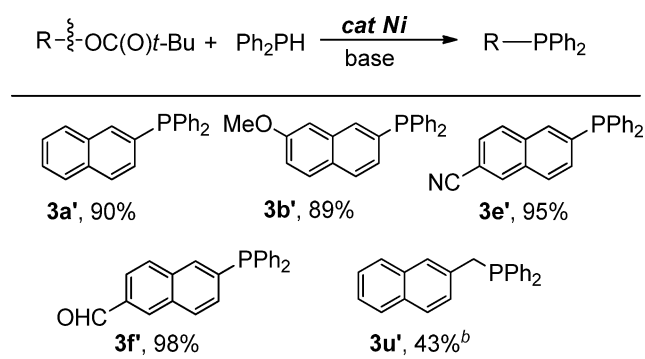
<sup>a</sup>Reaction conditions: 1 mmol of pivalate **1**, 1 mmol of P(O)H compound **2**, 10 mol % Ni(COD)<sub>2</sub>, 10 mol % dcype, 1 equiv of K<sub>2</sub>CO<sub>3</sub>, and 5 mL of dioxane were charged into a 10 mL sealed tube and heated at 80 °C for 18 h. <sup>b</sup>100 °C. <sup>c</sup>120 °C, 20 mol % Ni(COD)<sub>2</sub>, 20 mol % dcype, 2 equiv of K<sub>2</sub>CO<sub>3</sub>, and 8 mL of dioxane. <sup>d</sup>1.5 equiv of P(O)–H was added. <sup>e</sup>1.5 equiv of Cs<sub>2</sub>CO<sub>3</sub>, 8 mL of dioxane, 100 °C.

The generality of this coupling reaction was further demonstrated by using other esters as substrates. Alkenyl phosphonate **3t** (Table 2, entry 20) was prepared from the coupling with phenylethenyl pivalate (**1o**). In addition, benzylic (entries 21–25) and allylic (entry 26) esters could also be used as substrates to produce the corresponding coupling products in good to excellent yields. It should be noted that such a catalytic carbon–heteroatom bond-forming reaction via the activation of C(sp<sup>3</sup>)–O bonds has been rare until now.<sup>10a</sup>

Importantly, the substrates are not limited to the above-mentioned >P(O)H compounds, as even highly coordinative

secondary phosphines  $>P^{III}H$  could be used as the P–H source in this nickel-catalyzed C–O/P–H cross-coupling reaction to produce valuable P(III) phosphines directly in high yields. As shown in Table 3, naphthyl pivalates with either an electron-

Table 3. Ni-Catalyzed Coupling of Pivalates **1** with  $Ph_2PH^a$

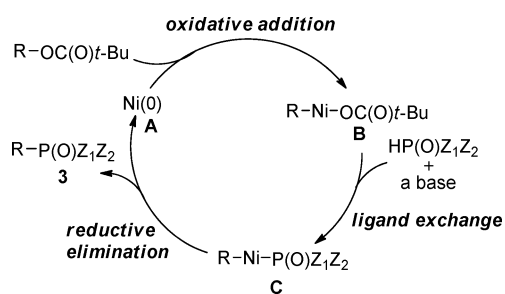


<sup>a</sup>Reaction conditions: 1 mmol of pivalate, 1 mmol of diphenylphosphine, 10 mol % Ni(COD)<sub>2</sub>, 10 mol % dcype, 1.0 equiv of K<sub>2</sub>CO<sub>3</sub>, and 5 mL of dioxane were charged into a 10 mL sealed tube and heated at 120 °C for 18 h. The product was isolated as a phosphine oxide by oxidation with H<sub>2</sub>O<sub>2</sub>. <sup>b</sup>1.5 equiv of Cs<sub>2</sub>CO<sub>3</sub>.

rich or electron-deficient group all were suitable for this cross-coupling reaction. For instance, both methoxy- and cyano-substituted naphthyl pivalates exhibited high reactivity with diphenylphosphine 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 diphenylphosphine to afford **3u'** in 43% yield under similar reaction conditions.

The mechanism is not fully understood. We propose that this Ni-catalyzed C–O/P–H cross-coupling takes place via the catalytic cycle shown in Scheme 2.<sup>14</sup> The Ni(0) species L–

Scheme 2. Proposed Mechanism for the Ni-Catalyzed C–O/P–H Cross-Coupling



Ni(0)–dcype (A), generated from Ni(COD)<sub>2</sub> 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 intermediate C. Finally, reductive elimination of C affords the coupling product **3** and regenerates the catalyst A.

In conclusion, we have developed an efficient Ni-catalyzed inert C–O/P–H cross-coupling that affords high yields of organophosphorus compounds under mild conditions. A variety of 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 that this

is a new general protocol for the construction of valuable C–P bonds from readily available, environmentally benign chemical sources. Work along this line, including scope, limitation, and mechanistic studies, is currently underway.

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed experimental procedures, spectral data for all compounds, and copies of <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>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 interest.

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(12) **3a'** could be quantitatively oxidized to **3a** upon heating under air. It was thought that **3'** was probably generated from the cross-coupling of **1a** with Ph<sub>2</sub>PH formed by the disproportionation of diphenylphosphine oxide.

(13) However, the reactions of the corresponding compounds PhOC(O)*t*-Bu and related progressed sluggishly under similar conditions and produced low yields of the products (ca. 10%).

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