# Nickel(II)-Magnesium-Catalyzed Cross-Coupling of 1,1-Dibromo-1-alkenes with Diphenylphosphine Oxide: One-Pot Synthesis of (*E*)-1-Alkenylphosphine Oxides or Bisphosphine Oxides

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**Abstract:** A novel nickel(II)-magnesium-mediated cross-coupling of diphenylphosphine oxide with a variety of 1,1-dibromo-1-alkenes has been developed, which provides a powerful and general methodology for the stereoselective synthesis of various (E)-1-alkenylphosphine oxides or bisphosphine oxides, with operational simplicity of the procedure, good to high yields and broad substrate applicability. Mechanistic studies reveal that the reaction might involve a Hirao reduction, cross-coupling and Michael addition.

**Keywords:** (*E*)-1-alkenylphosphine oxides; bisphosphine oxides; 1,1-dibromo-1-alkenes; DFT calculations; nickel(II)-magnesium catalysis

Transition metal-catalyzed carbon-phosphorus bond formation by cross-coupling reactions has attracted increasing attention in the last two decades due to its wide applicability in biological, pharmaceutical, material and catalytic sciences.<sup>[1]</sup> Alkenylphosphine oxides and bisphosphine oxides are important classes of phosphorus-containing, extremely valuable compounds in organic chemistry. For example, alkenylphosphine oxides are endowed with a wide-range of biological activities,<sup>[2]</sup> outstanding flame-retardant properties<sup>[3]</sup> and eminent metal-complexing abilities as ligands.<sup>[4]</sup> Furthermore, they can serve as useful precursors in the synthesis of a variety of synthetically elaborated bifunctional adducts by the ready addition of several nucleophiles to the double bond.<sup>[5]</sup> Bisphosphine oxides are used as organoextractions in hydrometallurgy,<sup>[6]</sup> and are key intermediates for the preparation of various valuable phosphine ligands<sup>[7]</sup> in homogeneous catalysis, organocatalysts for the allylation of *N*-acylhydrazones<sup>[8]</sup> and stereoselective direct aldol reactions of trifluoroethyl thioestesters.<sup>[9]</sup>

Recently, a few transition metal-catalyzed methods for the preparation of alkenylphosphine oxides have continuously emerged including the Pd-catalyzed cross-coupling of alkenyl halides with phosphine oxides,<sup>[10]</sup> olefin cross-metathesis,<sup>[11]</sup> Cu-catalyzed de-carboxylative coupling,<sup>[12]</sup> cleavage of silylepoxides<sup>[13]</sup> or stannyloxiranes<sup>[14]</sup> with lithium diphenylphosphide, hydrophosphination of terminal alkynes with diphosphines and hydrosilanes in the presence of oxygen,<sup>[15]</sup> Rh-catalyzed reaction of 1-alkynylphosphines with water,<sup>[16]</sup> in situ reactions of functionalized monoylides with carbonyl compounds<sup>[17]</sup> and transition metal-catalyzed addition of P(O)H compounds to alkynes.<sup>[18,20]</sup> Bisphosphine oxides can be prepared by several methods such as the Pd-<sup>[18f,19]</sup> or Rh-catalyzed<sup>[20]</sup> double hydrophosphinylation of alkynes, substitution reactions of 1,2-dichloride complex,<sup>[21]</sup> double nucleophilic addition of secondary phosphine oxides to methylacetylene,<sup>[22]</sup> Kolbe electrolytic coupling reactions of phosphinoyl-acetic or propanoic acids<sup>[23]</sup> and catalytic olefin cross- or homo-metathesis.<sup>[11,24]</sup> However, these traditional procedures suffer from relatively strict reaction conditions, low selectivity, poor substrate scope or unsatisfactory yield, and there is still a strong need for developing more convenient and efficient approaches to alkenvlphosphine oxides and bisphosphine oxides. It is extremely worthwhile to develop highly efficient methods to prepare

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alkenylphosphine oxides and bisphosphine oxides from 1,1-dibromo-1-alkenes as starting materials because 1,1-dibromo-1-alkenes are important and readily available building blocks,<sup>[25]</sup> which can be conveniently prepared by Corey-Fuchs reaction.<sup>[26]</sup> Herein we disclose a novel methodology for the highly efficient preparation of stereoselective (E)-1-alkenylphosphine oxides or bisphosphine oxides from readily available 1,1-dibromo-1-alkenes and diphenylphosphine oxide through Ni(II)-Mg-mediated cross-coupling with the advantages of operational simplicity of the procedure, good to high yields and broad substrate applicability (Scheme 1). To the best of our knowledge, this method is the first example of a Ni(II)-Mg-mediated cross-coupling of 1,1-dibromo-1-alkenes with diphenylphosphine oxide leading to (*E*)-1-alkenylphosphine oxides or bisphosphine oxides.

Initially, we chose 2,2-dibromovinylbenzene (1a) and  $Ph_2P(O)H$  as the model substrates to optimize the catalysis conditions. When a mixture of 1a (0.30 mmol), $Ph_2P(O)H$ (0.66 mmol), NiCl<sub>2</sub> (0.03 mmol), 2,2'-bipyridine (bpy, 0.06 mmol), K<sub>3</sub>PO<sub>4</sub> (1.80 mmol) in THF was heated at 70°C overnight under dry argon, only a trace amount of product was obtained. However, when Zn or Mg (0.30 mmol) was added to the reaction system, the reaction yields were greatly improved and alkenylphosphine oxide 2a was formed in 78% or 84% yield with high stereoselectivity (E/Z=92/8, 92/8), respectively. A screening of the catalysts showed that Ni(II) salts, especially NiBr<sub>2</sub>, was found to be the most effective catalyst to generate the desired product 2a. Catalysts (10 mol%) and corresponding yields of 2a were as follows: NiBr<sub>2</sub>, 88%; Ni(OAc)<sub>2</sub>, 77%; Ni(acac)<sub>2</sub>, 80% and Ni(NO<sub>3</sub>)<sub>2</sub>, 82%. Under similar reaction conditions, other metal salts, such as AgI, CuBr and FeCl<sub>2</sub>, did not or only sluggishly promoted this reaction. No obvious change in yield was observed when the loading of Mg was increased to 2.0 equiv. Ligand screening showed that bpy was the best choice. The type of solvent was vital to the present catalytic reaction. Besides THF (88%) and DMF (66%), other solvents including toluene, dioxane, CH2Cl2 and MeCN, produced only a trace amount of product 2a. Bases also highly affected this reaction: KOH, 0%;  $Cs_2CO_3$ , 20%;  $K_2CO_3$ , 38%; and  $Et_3N$ , 0%.

Under the optimized conditions shown in footnote [a] of Table 1, we next surveyed the cross-coupling of various substituted 1,1-dibromo-1-alkenes with diphenylphosphine oxide to understand the scope of the reaction. As demonstrated in Table 1, the corresponding coupling products were produced in moderate to good yields with high stereoselectivity in favor of the (E)-isomer. When a variety of electron-withdrawing or electron-donating groups was introduced on the phenyl ring of the 1,1-dibromo-1-alkenes, the results illustrated that electronic effects and steric hindrance are not operative in this coupling reaction (Table 1, entries 2-11, 19). Notably, heterocycle-substituted 1,1dibromo-1-alkenes were also found to be suitable reaction partners, and the corresponding coupling products were obtained in good yields (Table 1, entries 12-14). However, aliphatic 1,1-dibromo-1-alkenes gave lower yields than aromatic ones (Table 1, entries 17 and 18), for example, the coupling of diphenylphosphine oxide with 2,2-dibromovinylbenzene (1a) afforded an 88% isolated yield, whereas 1,1-dibromonon-1-ene (1q) showed lower reactivity under the same conditions and provided a 66% yield. 1,1-Dibromoprop-1-en-2-yl)benzene (1s) could also be used as the substrate to give the desired product in 90% yield (entry 19). Gratifyingly, the present catalytic reaction was also successfully applied to the coupling of 1,4bis(2,2-dibromovinyl)benzene (1t) with diphenylphosphine oxide and predominantly furnished the (E)isomer in 70% yield (entry 20). In regard to the reactant, in addition to diphenylphosphine oxide, H-phosphonate diesters could also be used as the substrates, generating the corresponding products in moderate yield. For example, the coupling of diethyl and diisophosphonate with 1,1-dibromo-1-alkenes propyl under similar reaction conditions could proceed smoothly, giving 70% and 74% yield and high stereoselectivity for E/Z = 94/6 and 94/6 isomers, respectively (for details see the Supporting Information). Obviously, this approach affords a strong tool for the preparation of the valuable P-alkenylated motifs.

It is noticeable that this procool could also be used in the synthesis of enantiomerically pure P-chiral alkenvlphosphinate  $3b^{[27]}$  from optically pure H-phosphi-



Scheme 1. Ni(II)-Mg-catalyzed one-pot preparation of (E)-1-alkenylphosphine oxides or bisphosphine oxides.

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	$R \xrightarrow{Br} H \xrightarrow{H}$	)  _Ph Ph	NiBr <sub>2</sub> , Mg, 70 °C	O │ P_Ph ◇ P_Ph		
Entry	Br 1 Substrate		Product	2	F/7[c]	Yield <sup>[b]</sup>
1	Br 1a	a	P(0)Ph <sub>2</sub>	a	92/8	88%
2		b	P(0)Ph <sub>2</sub>	b	93/7	85%
3	Br 10	c	P(O)Ph <sub>2</sub> 2	c	92/8	88%
4	F Br 10	d	P(0)Ph <sub>2</sub> 2	d	90/10	77%
5	CI Br 10	e	CI P(O)Ph <sub>2</sub>	e	94/6	82%
6	Br Br 11	f	Br P(O)Ph <sub>2</sub> 2	F	93/7	80%
7	F <sub>3</sub> C Br 1	g	F <sub>3</sub> C	g	95/5	84%
8	MeO <sub>2</sub> C Br 11	h	MeO <sub>2</sub> C P(O)Ph <sub>2</sub>	h	90/10	85%
9	NC CI Br 1i	i	NC CI	i	94/6	78%
10	Br 1j	j	P(O)Ph <sub>2</sub> 2	j	92/8	75%
11	MeO Br 11 MeO	k	MeO CI P(O)Ph <sub>2</sub> MeO 2	k	92/8	85%
12		I	P(O)Ph <sub>2</sub> 2	I	91/9	70%
13	S Br 11	m	P(O)Ph <sub>2</sub> 2	m	96/4	80%
14		n		n	93/7	72%
15	Br 1	0	2	0	95/5	90%
16	Br 1	p	P(O)Ph <sub>2</sub> 2	þ	94/6	72%
17	Me Br 10	q	$Me_{0} P(O)Ph_2 2$	q	91/9	66%
18	Br 1	r	P(O)Ph <sub>2</sub>	r	91/9	68%
19	Br 1	s	P(O)Ph <sub>2</sub>	s	90/10	90%
20 <sup>[d]</sup>	Br Br 11	t	P(O)Ph <sub>2</sub> Ph <sub>2</sub> (O)P	( <i>E</i> ,	<i>⊑/E,∠/∠,∠)</i> 91/9/0	70%

Table 1. Ni(II)-Mg-catalyzed one-pot preparation of (E)-1-alkenyl-phosphine oxides.<sup>[a]</sup>

<sup>[a]</sup> Reaction conditions: **1** (0.50 mmol), Ph<sub>2</sub>P(O)H (1.10 mmol), NiBr<sub>2</sub> (0.05 mmol), Mg (0.5 mmol), bpy (0.10 mmol), K<sub>3</sub>PO<sub>4</sub> (3.0 mmol), THF (2.5 mL), 70 °C, 3 h.

<sup>[b]</sup> Isolated yield.

<sup>[c]</sup> Defined by *in situ* <sup>1</sup>H NMR or <sup>31</sup>P NMR.

<sup>[d]</sup> The amount of other reagents doubled except for **1**, 5 h.

nate  $3a^{[28]}$  with retention of configuration at the phosphorus atom (Scheme 2).

More interestingly, the bisphosphine oxides were produced through increasing the amount of  $Ph_2P(O)H$  to 3.2 equiv. (Table 2). This one-pot reac-



81% E/Z=81/19

**Scheme 2.** Ni(II)-Mg-catalyzed cross-coupling of **1a** with optically pure H-phosphinate **3a**.

tion performed quite well for all the substrates examined, and the desired bisphosphine oxides were obtained in good to excellent yields. The results indicated that aromatic 1,1-dibromo-1-alkenes showed better reactivity than aliphatic ones (Table 2, entries 1 and 3). It is noteworthy that cinnamaldehyde-derived 1,1dibromoalkenes (1u) underwent the reaction to produce the 1,4-addition product 4b with good yield and high selectivity for the (E)-isomer (94/6, entry 2). However, under similar reaction conditions, H-phosphonate diester as substrate did not afford the desired bisphosphonate product.

To gain more insight into the reaction mechanism, the catalytic pathway has been investigated in detail using a combination of experiments and density functional theory (DFT) calculations. When substrate 1a was treated with 3 equiv. of Ph<sub>2</sub>P(O)H and 6 equiv. of K<sub>3</sub>PO<sub>4</sub> in the absence of NiBr<sub>2</sub>/Mg catalyst, only 2bromovinylbenzene (E/Z=92/8) was produced after stirring at 70°C in THF for 10 h (Scheme 3), clearly demonstrating that the configuration of diphenyl-(styryl)phosphine oxide (2a) (E/Z=92/8) was determined by that of the product of a Hirao-type reduction,<sup>[29]</sup> and the Ni(II)-Mg catalyst played the key role in the next coupling step. The Michael addition of diphenyl(styryl)phosphine oxide (2a) with 1.5 equiv. of  $Ph_2P(O)H$  and 5 equiv. of  $K_3PO_4$  without a metal catalyst was investigated and the double-hydrophosphinylated product (4a) was obtained in excellent yield (96%). These results illustrated that the coupling step was metal-catalyzed, and the addition step was promoted by the base.<sup>[30]</sup>

Based on the nickel- and palladium-catalyzed crosscoupling reaction mechanisms,<sup>[31]</sup> we proposed a possible mechanism of the Ni(II)-Mg catalyzed cross-coupling step. The active catalytic species **IN0** was produced from the catalyst precursor NiBr<sub>2</sub> in the presence of reducing magnesium powder and bpy. The approach of (*E*)-(2-bromovinyl)benzene toward **IN0** leads to the formation of the  $\eta^2$  complex **IN1**. Oxida-

Table 2. Ni(II)-Mg-catalyzed one-pot synthesis of bisphosphine oxides.<sup>[a]</sup>

	$R \xrightarrow{Br} H \xrightarrow{O} H \xrightarrow{H-P} Ph$	2,2	NiBr₂, Mg, 70 °C Pł '-bipyridine, K₃PO₄,THF Ph	O h∖⊟ n∕P R	O II_Ph P_Ph 4	
Entry	Substrate		Product		Time	Yield <sup>[b]</sup>
1	Ph Br	1a	Ph <sub>2</sub> (O)P Ph	4a	8 h	90%
2	Ph Br Br	1u	Ph <sub>2</sub> (O)P Ph	4b	12 h	82% (94/6) <sup>[c]</sup>
3	Me () <sub>6</sub> Br Br	1q	$\begin{array}{c} Ph_2(O)P & P(O)Ph_2\\ Me(\overset{\frown}{\searrow}_5 & P(O)Ph_2 \\ \end{array}$	4c	10 h	70%
4 <sup>[d]</sup>	Br Br	r 1v	Ph <sub>2</sub> (O)P P(O)Ph <sub>2</sub> Ph <sub>2</sub> (O)P P(O)F	<sup>p</sup> h <sub>2</sub> <b>4d</b>	15 h	85%

[a] Reaction conditions: 1 (0.50 mmol), Ph<sub>2</sub>P(O)H (1.60 mmol), NiBr<sub>2</sub> (0.05 mmol), Mg (0.5 mmol), bpy (0.10 mmol), K<sub>3</sub>PO<sub>4</sub> (3.0 mmol), THF (3.0 mL), 70 °C.

<sup>&</sup>lt;sup>[b]</sup> Isolated yield.

<sup>&</sup>lt;sup>[c]</sup> E/Z was defined by *in situ* <sup>1</sup>H NMR.

<sup>&</sup>lt;sup>[d]</sup> The amount of other reagents doubled except for **1**, 5 h.



Scheme 3. Mechanistic studies.

tive addition of **IN1** proceeds through a three-membered-ring transition state **TS1**. The free energy of **TS1** is +14.4 kcalmol<sup>-1</sup> higher than that of **IN1**, indicating that oxidative addition is a facile step. The immediate product of oxidative addition, a four-coordinated Ni(II) complex **IN2**, is more stable than **IN0** by -35.4 kcalmol<sup>-1</sup>. Subsequent ligand exchange with diphenylphosphinite generates a Ni(II) species **IN3** with a negative energy of -9.9 kcalmol<sup>-1</sup>. From **IN3** a three-membered ring transition state **TS2** is indentified for the reductive elimination. The overall barrier from **IN3** to **TS2** is computed to be 25.6 kcalmol<sup>-1</sup>. The calculated results indicate that the first two steps are barrierless processes, and the rate-determining step is the C–P bond formation, in line with the experimental observation that the Ni-Mg-catalyzed reaction was carried out at 60–70 °C.<sup>[32]</sup> The structure of the corresponding transition state is shown in Scheme 3 (hydrogens are not shown for clarity). It is interesting to note that the plotted highest occupied molecular orbital (HOMO) shows bonding interaction between the *d*-orbital of Ni and *p*-orbital of P and Nibonded C atoms (Figure 1). The contribution from other carbons on the phenyl ring of 1,1-dibromo-1alkenes to the HOMO is very small, in accord with the experimental results that both electron-withdrawing and electron-donating groups on the aromatic 1,1dibromo-1-alkenes have no evident effect on the C–P bond formation.



**Figure 1.** The HOMO (isovalue = 0.04) of the located **TS2** by DFT calculations.

In summary, we have successfully developed a simple and highly efficient method for the synthesis of (E)-1-alkenylphosphine oxides or bisphosphine oxides through direct coupling of readily available 1,1-dibromo-1-alkenes with diphenylphosphine oxide under mild reaction conditions. This cross-coupling is firstly performed under catalysis of commercially available and inexpensive Ni(II)-Mg catalyst system, and various valuable products can be conveniently obtained in a one-pot process. Preliminary mechanistic studies indicate that this reaction might involve a Hirao-type reduction, Ni(II)-Mg-catalyzed crosscoupling and Michael addition. Further mechanistic details and synthetic applications are currently underway.

# **Experimental Section**

#### General Procedure for the Synthesis of 2a-2t and 3b

For 2a–2s: an oven-dried Schlenk tube containing NiBr<sub>2</sub> (0.05 mmol), Mg (0.50 mmol), bpy (0.10 mmol), Ph<sub>2</sub>P(O)H (2a–2s) (1.10 mmol), K<sub>3</sub>PO<sub>4</sub> (3.0 mmol), and 1,1-dibromo-1-alkene (0.50 mmol) was evacuated and purged with argon three times. Freshly distilled THF (2.5 mL) was added at room temperature, and then the resulting mixture was stirred at 70 °C for the indicated time. After completion of the reaction, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, petroleum ether-EtOAc or CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH).

*For 2t:* the amount of other reagents was doubled except for **1t**.

*For 3b:* **3a** (1.10 mmol) replaced  $Ph_2P(O)H$ , at 60 °C.

### General Procedure for the Synthesis of 4a-4d

**For 4a–4c:** an oven-dried Schlenk tube containing 1,1-dibromo-1-alkene (0.50 mmol),  $Ph_2P(O)H$  (1.60 mmol),  $NiBr_2$ (0.05 mmol), Mg (0.50 mmol), bpy (0.10 mmol) and  $K_3PO_4$ (3.0 mmol) was evacuated and purged with argon three times. Freshly distilled THF (3.0 mL) was added at room temperature, and then the resulting mixture was stirred at 70 °C for the indicated time. The crude product was purified by the procedure described above.

For 4d: the amount of other reagents doubled except 1v.

#### **Computational Methods**

All the calculations were performed with the Gaussian 03 programs.<sup>[33]</sup> The gas phase geometries of all compounds were optimized without any constraint by the density functional theory (DFT) method B3LYP. The 6-31+G(d) basis set was used for C, H, N, O, P. Polarization functions were added for Br ( $\xi_d = 0.428$ ) and Ni ( $\xi_f = 3.130$ ) to the standard LANL2DZ basis set.<sup>[34]</sup> Frequency analysis was performed after optimization to verify the minima and transition states. Intrinsic reaction coordinate (IRC) calculations of the transition states were performed to confirm that the transition states were located on the real saddle points of the reaction potential energy surfaces. For compounds that had multiple conformations, efforts were made to find the lowest-energy conformation by comparing the structures optimized from different starting geometries. Single-point electronic energies were calculated by using the B3LYP method. The  $SDD^{[35]}$  basis set was used for Ni and 6-311+G(2d, p) was used for other atoms. The Gibbs free energy correction from frequency calculation was added to the single-point energy to obtain the Gibbs free energy. To calculate the solvation energies, the IEF-PCM method with the UA0 radii was used. The gas-phase geometry was used for all of the solution phase calculations. The solvation free energy was added to the gas-phase free energy to obtain the Gibbs free energy in solution. All the solution-phase free energies reported in the paper correspond to the reference state of 1 mol/L, 298 K.

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