COMMUNICATION

Experimental and theoretical studies on nickel–zinc-catalyzed cross-coupling of *gem*-dibromoalkenes with P(O)−H compounds†

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A new stereoselective one-pot protocol for the preparation of *E*-alkenyl-phosphorus compounds under catalysis of an inexpensive nickel–zinc catalyst system has been developed, which provides a potential useful method for C−P bond formation. ^{31}P NMR spectrum and density functional theory calculations were performed to study the reaction mechanism.

The rapid development of new methods for carbon–carbon (C–C) and carbon-heteroatom (C–X) bond formation is a critical challenge in modern organic chemistry owing to the synthesis of functional molecules, such as biologically active compounds and natural products.[1] In this regard, the transition-metal-catalyzed cross-coupling reactions are very useful protocols for the construction of structurally sophisticated compounds over the past years.[2] Organophosphorus compounds are an important class of chemicals, which are extensively used in pharmaceuticals and material sciences.[3] Particularly, alkenyl-phosphorus compounds have attracted more attention due to their prime properties. For example, in addition to their eminent metal-complexing abilities[4] and flame-retardants or copolymers[5] in polymer science, several nucleophiles, such as alcohols,[6] thiols,[7] amines,[8] phosphines[9] and carbanion species,[10] can readily add to the olefinic bond to provide potential useful bifunctional adducts, which could be further synthetically elaborated.

Recently, a number of transition-metal mediated methods for the synthesis of alkenyl-phosphorus compounds have been continuously emerged.[11] For instance, in 2009,

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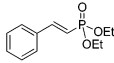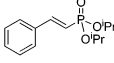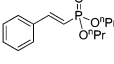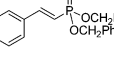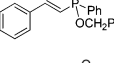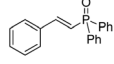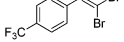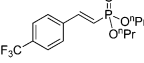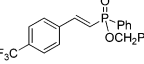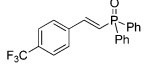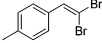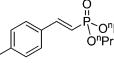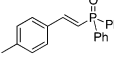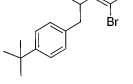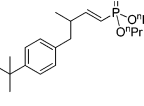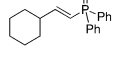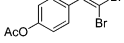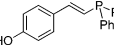
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Djakovitch and co-workers reported a Pd-catalyzed Heck reaction for synthesis of diethyl 2-(aryl)vinylphosphonates.[11a] Very recently, Yang, Liang and co-workers described a copper-catalyzed C–P coupling through decarboxylation.[11b] However,
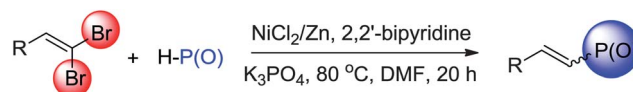
Scheme 1 Ni(II)−Zn-catalyzed one-pot synthesis of alkenyl-phosphorus compounds.

Table 1 Optimization of reaction condition[a]

Entry	Catalyst	Ligand	Solvent	Base	Yield[b] (%)
1	NiCl₂	L1	DMF	K₃PO₄	18
2	NiCl₂/Zn	L1	DMF	K₃PO₄	60
3[c]	NiCl₂/Zn	L1	DMF	NEt₃	n.d.
4	NiCl₂/Zn	L1	DMF	K₂CO₃	38
5[c]	NiCl₂/Zn	L2	DMF	K₃PO₄	n.d.
6	NiCl₂/Zn	**L3**	**DMF**	K₃PO₄	88
7[c]	NiCl₂/Zn	L4	DMF	K₃PO₄	n.d.
8	NiCl₂/Zn	L3	Toluene	K₃PO₄	0
9	NiCl₂/Zn	L3	THF	K₃PO₄	70
10	NiCl₂/Zn	L3	dioxane	K₃PO₄	10
11	NiCl₂/Zn	L3	H₂O	K₃PO₄	0
12[c]	—	—	DMF	K₃PO₄ or NEt₃	n.d.

[a] *Reaction conditions*: **1a** (0.2 mmol), **2b** (0.44 mmol), NiCl₂ (0.02 mmol), Zn powder (0.4 mmol), ligand (0.04 mmol), base (1.0 mmol), solvent (2.0 mL), 80 °C, 20 h. [b] Isolated yield. [c] Only reduced product was detected. n.d. = no detected.

most of these methods lack satisfactory yield, high stereo-selectivity or relatively mild reaction conditions. Herein, our ongoing interests in nickel and organophosphorus chemistry[12,9c,11g] led us to investigate a new procedure for the synthesis of 1-alkenylphosphonates, 1-alkenylphosphinates or 1-alkenylphosphine oxides both experimentally and theoretically (Scheme 1).

In our initial study, 2,2-dibromovinyl benzene (1a, 0.2 mmol) was treated with diisopropyl phosphonate (2b, 0.44 mmol) in DMF at 80 °C under catalysis of $NiCl_2$ (0.02 mmol), N^1,N^2-dimethylethane-1,2-diamine (L1, 0.04 mmol) and K_3PO_4 (1.0 mmol) system (Table 1). Unfortunately, the desired product 3b, was obtained in only 18% yield (Table 1, entry 1). Drawing inspiration from our experience in nickel(II) catalysis,[9c,12d] we

Table 2 Reaction of *gem*-dibromoalkenes with P(O)H compounds[a]

Entry	Substrate		Product		Yield[b] (%)	E/Z[c]
1	1a	2a		3a	82	96/4
2	1a	2b		3b	88	96/4
3	1a	2c		3c	88	95/5
4	1a	2d		3d	86	98/2
5	1a	2e	—		0	—
6	1a	2f		3e	81	95/5
7	1a	2g		3f	72	94/6
8	1b	2c		3g	78	97/3
9	1b	2f		3h	72	91/9
10	1b	2g		3i	74	94/6
11	1c	2c		3j	80	97/3
12	1c	2g		3k	77	94/6
13	1d	2c		3l	54	90/10
14	1e	2g		3m	56	89/11
15	1f	2g		3n	66	88/12

[a] *Reaction conditions*: 1 (0.2 mmol), 2 (0.44 mmol), $NiCl_2$ (0.02 mmol), Zn powder (0.4 mmol), L3 (0.04 mmol), K_3PO_4 (1.0 mmol), DMF (2.0 mL), 80 °C, 20 h. [b] Isolated yield. [c] Defined by ¹H NMR. n.d. = no detected.

chose Zn powder (0.4 mmol) as the reducing agent to test this reaction. We were pleased to find that NiCl$_2$/Zn greatly improved the yield to 60%.[13] Base screening showed that K$_3$PO$_4$ was the best choice (Table 1, entries 2–4). The type of ligands was very crucial to the present reaction (Table 1, entries 2 and 5–7). For example, when N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (**L2**) or N,N-dimethylpyridin-4-amine (**L4**) was chosen as the ligand, no expected product could be detected in the crude reaction mixture. Gratifyingly, 2,2′-bipyridine (**L3**) exhibited an excellent catalytic performance and gave the desired product **3b** in 88% yield. Next, a screening of the solvent showed that besides DMF (88%) and THF (70%), other solvents provided only a trace amount of **3b** (Table 1, entries 6 and 8–11). It is important to note that only the reduced product (2-bromovinyl)benzene could be detected without the presence of NiCl$_2$/Zn (Table 1, entry 12).[14]

To test the scope of the reaction, we next explored the one-pot protocol of various P(O)H compounds with **1a** as shown in Table 2. In addition to H-phosphonate diesters (Table 2, entries 1–4), H-phosphinate esters and diphenylphosphine oxides (Table 2, entries 6 and 7) all could be efficiently coupled with **2a** to afford the corresponding alkenyl-phosphorus compounds in good isolated yields in favor of the E-isomer. Note that diphenyl phosphonate **2e** was found to be unsuitable reaction partner since it might be hydrolyzed under the alkaline condition (Table 2, entry 5).[15] gem-Dibromoalkenes with the electron-rich substituent (p-Me) or electron-deficient substituent (p-CF$_3$) all gave good yields with high stereoselectivity (Table 2, entries 8–12). For instance, 1-(2,2-dibromovinyl)-4-(trifluoromethyl)-benzene (**1b**) and 1-(2,2-dibromovinyl)-4-methylbenzene (**1c**) coupled with dipropyl phosphonate (**2c**), giving the desired products in 78% and 80% isolated yields in favor of the E-isomer, respectively. Gratifyingly, aliphatic gem-dibromoalkenes participated in the reaction, providing the corresponding E-alkenyl-phosphorus compounds with moderate yields (Table 2, entries 13 and 14). 4-(2,2-Dibromovinyl)phenyl acetate (**1f**) reacted with **2g**, concomitant with hydrolyzation, providing **3n** in 66% yield (Table 2, entry 15). Therefore, undoubtedly, this Ni–Zn-catalyzed coupling is a general and practically useful method for the synthesis of E-1-alkenyl-phosphonates, E-1-alkenylphosphinates or E-1-alkenylphosphine oxides.

Fig. 2 Proposed mechanism.

To investigate the mechanism of the Hirao reduction,[14] we decided to trace the reaction by ^{31}P NMR spectroscopy, which has been successfully applied in studying various phosphorus-containing reactions.[16] A mixture of **1a** (0.15 mmol), diethyl phosphonate (**2a**, 0.30 mmol) and triethylamine (0.30 mmol) in dry DMF was followed by ^{31}P{H} NMR spectroscopy (Fig. 1). Initially, only one signal was assigned to diethyl phosphonate (δ_a = 7.8 ppm). Sixty minutes later, two new phosphorus-containing species, intermediate b and byproduct c, were detected (δ_b = 19.0 ppm and δ_c = −12.5 ppm), which indicated the formation of the P–C and P–Br bonds,[10d,17] respectively. Then, the peak of b was decreasing while that of **c** was increasing over time. The reaction reached the thermodynamic equilibrium in approximately 180 minutes.[18]

A possible mechanism is proposed based on above ^{31}P NMR spectrum analysis and previous reports (Fig. 2).[19] Firstly, the reaction of tetracoordinated R$_2$P(O)H with a base generates a three coordinated R$_2$PO$^-$,[19c] which would add to the olefinic bond of gem-dibromoalkenes and followed by protonation to give the intermediate **b**. Next, two possible pathways are considered (Fig. 2A and B). Both processes involves elimination of R$_2$P(O)Br (**c**) species, leading to the product of the Hirao-type reduction. In order to explain why Hirao-type reduction favoured E-isomer, density functional theory (DFT) calculations

Fig. 1 The stack ^{31}P{H} NMR spectra.
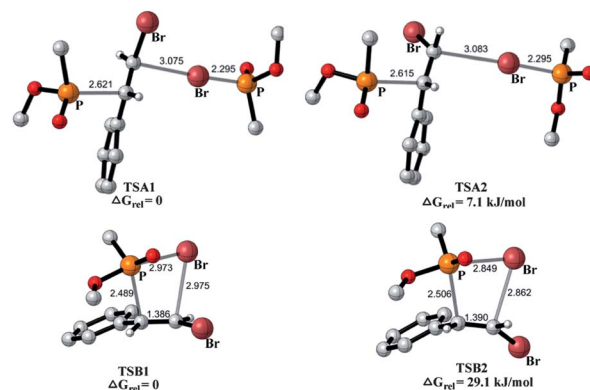
Fig. 3 Transition state structures.[23] For clarity, some C−H hydrogen atoms are not shown. Bond lengths are in Å.
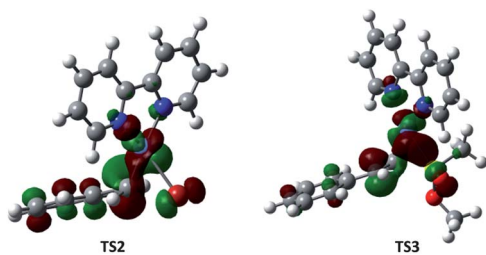
Fig. 4 The HOMOs (isovalue = 0.04) of the located transition states by DFT calculations.

were carried out.[20] The model substrate methyl methyl-phosphinate (Me)(MeO)P(O)H and (2,2-dibromovinyl)benzene (**1a**) were chosen. Relative free energies in solution are employed to analyze the reaction mechanism. From intermediate b, four transition states (**TSA1**, **TSA2**, **TSB1** and **TSB2**) were identified (Fig. 3). **TSA1** and **TSB1** connect the *E*-isomer while **TSA2** and **TSB2** lead to formation of the *Z*-isomer. Gratifyingly, the calculation results indicate that the free energies of **TSA1** and **TSB1** are relatively lower than those of **TSA2** and **TSB2** by 7.1 kJ mol^{-1} and 29.1 kJ mol^{-1}, respectively, thus suggesting that the formation of *E*-isomer is kinetically favorable. The proposed cross-coupling process includes three basic steps (oxidative addition, ligand exchange and reductive elimination) as exemplified by several recent studies.[1a,b,12d,20] DFT calculations reveal that the barriers of oxidative addition and reductive elimination are 60.9 and 116.4 kJ mol^{-1}, respectively.[21] Thus, the reductive elimination is the rate-determining step, in accord with the experimental results that this reaction was performed at 80 °C.[22] Interestingly, the plotted highest occupied molecular orbitals (HOMO) of the located transition states of oxidative addition (**TS2**) and reductive elimination (**TS3**) steps reveal that the bonding interaction can mainly be attributed to the d-orbital of Ni and p-orbital of Ni bonded carbons (Fig. 4). While other carbons on the aromatic ring of *gem*-dibromoalkenes contribute relatively little to the HOMOs, in line with the experimental observations that both electron-donating (*p*-CH$_3$) and electron-withdrawing (*p*-CF$_3$) groups on the phenyl ring of *gem*-dibromoalkenes have no evident effect on this transformation.

In summary, we have developed a mild, operationally simple, and high-efficient one-pot protocol for the stereo-selective preparation of *E*-1-alkenylphosphonates, *E*-1-alkenyl-phosphinates or *E*-1-alkenylphosphine oxides under catalysis of inexpensive and commercially available nickel–zinc catalyst system. Mechanistic studies show that this one-pot reaction might involve Hirao-type reduction and Ni–Zn-catalyzed cross-coupling. The proposed plausible mechanism is supported by the ^{31}P NMR spectrum analyses and DFT calculations. Further synthetic applications and mechanistic investigation of this method are currently underway.

Experimental procedure

An oven-dried Schlenk tube containing NiCl$_2$ (0.02 mmol), Zn powder (0.4 mmol), 2,2′-bipyridine (0.04 mmol), P(O)H (0.44 mmol), *gem*-dibromoalkenes (0.2 mmol) and K$_3$PO$_4$ (1.0 mmol) was evacuated and purged with argon three times. Dry DMF (2.0 mL) was added at room temperature, and the resulting mixture was stirred at room temperature for 30 minutes. Then the mixture was heated at 80 °C for 20 hours. The mixture was cooled to room temperature and then transferred to a round-bottom flask. Silica gel (3.0 g) was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dry-loaded onto a silica gel column and purified by flash chromatography to yield the desired product.

Acknowledgements

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