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Copper-Catalyzed Direct Twofold C−P Cross-Coupling of Unprotected Propargylic 1,4-Diols: Access to 2,3-Bis(diarylphosphynyl)-1,3-butadienes

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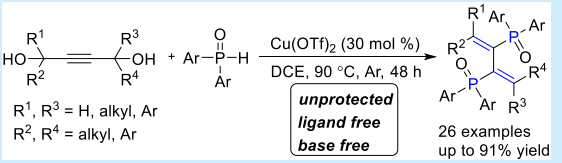
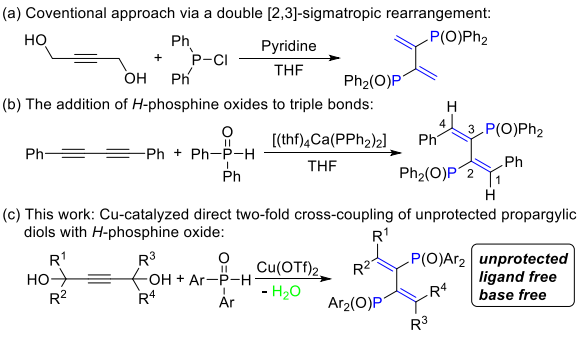
Supporting Information

ABSTRACT: The first facile and efficient Cu-catalyzed direct coupling of unprotected propargylic diols with *H*-phosphine oxides was developed, providing a practical approach to access structurally diverse 2,3-bis(diarylphosphynyl)-1,3-butadienes along with the formation of two new P−C_{sp^2} and two new C═C bonds under ligand- and base-free conditions.



Organophosphorus compounds have attracted continuous attention for synthetic chemists in recent decades due to their broad applicability in organic synthesis, medicinal chemistry, and materials science.[1] Among them, 2,3-bis(diarylphosphinyl)-1,3-butadienes are an important class of butadiene-containing, valuable building blocks with wide applications in synthetic chemistry.[2] Moreover, various useful bidentate chiral ligands[3] could be easily prepared by asymmetric hydrogenation of these motifs as a type of chelating diphosphorus system, which were widely used in ligand chemistry.[4] However, to date, the synthetic method for the synthesis of this class of 2,3-bis(diphenylphosphinyl)-1,3-butadienes is rather rare and only two methods are reported.[5] One includes using a double [2,3]-sigmatropic rearrangement from 2-butyne-1,4-diol and air- and moisture-sensitive chlorodiphenylphosphine as starting materials afforded the corresponding 2,3-bis(diphenylphosphinyl)-1,3-butadiene product (Scheme 1a), which was discovered in the early 1980s and still used in the synthesis of this motif to date. Yet, it is greatly limited to the use of unstable and toxic phosphorus chlorides along with the need for excess bases and poor functional group compatibility, thus limiting its application.[5a] Additionally, transition-metal-catalyzed addition reaction of a P(O)−H bond to the triple bond has been one of the most straightforward methodologies for the preparation of vinylphosphonates in recent years.[6] Based on this strategy, Westerhausen's group reported an example of calcium-mediated hydrophosphanylation of 1,4-diphenylbuta-1,3-diyne with diphenylphosphine oxide leading to a 1,3-butadiene product (Scheme1b), but this transformation suffered from the commercially unavailable and air-sensitive calcium catalyst and could not prepare multisubstituted 1,3-butadienes containing two substituents at the C1 or C4 position,[5b] which restricted their further study. Therefore, developing a general, economic, and efficient strategy to access highly substituted and novel 2,3-bis(diarylphosphinyl)-1,3-butadienes starting from readily available substrates under base- and ligand-free conditions remains highly desirable.

Scheme 1. Some Synthetic Strategies to 1,3-Diene Frameworks



Over the past few years, transition-metal-catalyzed direct cross-coupling of propargylic 1,4-diols for selective C−C and C−heteroatom bond formation has emerged as one of the most promising and significant strategies for the construction of complex molecular frames in modern organic synthesis because of its avoidance of the protection of reaction partners and its prominent advantages of step and atom economy and environmental sustainability.[7] On the other hand, the stable and readily available propargylic 1,4-diols as starting substrates are highly attractive for chemical synthesis from environmental and economic points of view since the water is the only byproduct in some transformations.[8] Thus, as an appealing alternative, a more synthetically useful procedure to highly substituted 2,3-bis(diarylphosphinyl)-1,3-butadienes would involve direct twofold C−P cross-coupling of unprotected propargylic 1,4-diols with *H*-phosphine oxides (Scheme 1c). Nevertheless, to the best of our knowledge, there is still no

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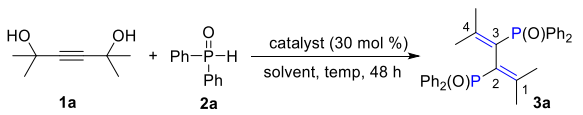
example of employing such an attractive and practical approach to access 2,3-bis(diarylphosphinyl)-1,3-butadiene compounds. As part of our ongoing efforts to develop environmentally friendly new methods for the P−C bond construction,[9] herein, we disclosed the first example of Cu-catalyzed direct twofold cross-coupling of propargylic diols with *H*-phosphine oxides to construct highly substituted 2,3-bis(diarylphosphinyl)-1,3-butadienes under ligand- and base-free conditions. This protocol enables a facile and efficient access to structurally diverse 2,3-bis(diarylphosphinyl)-1,3-butadiene frameworks along with the formation of two new P−C_{sp^2} and two new C═C bonds through a simple one-pot process.

Initially, our efforts focused on the model reaction of 2,5-dimethylhex-3-yne-2,5-diol (**1a**) with diphenylphosphine oxide (**2a**) to optimize the reaction conditions (Table 1). To our

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a

entry	catalyst	solvent	temp (°C)	yield (%)[b]
1	$Cu(OTf)_2$	DCE	80	62
2	$Fe(OTf)_3$	DCE	80	21
3	TfOH	DCE	80	30
4	$CuCl_2$	DCE	80	17
5	CuCl	DCE	80	10
6	$Zn(OTf)_2$	DCE	80	25
7	$Cu(OTf)_2$	CH_3CN	80	0
8	$Cu(OTf)_2$	THF	80	3
9	$Cu(OTf)_2$	CH_2Cl_2	80	55
10	$Cu(OTf)_2$	PhCl	80	5
11	$Cu(OTf)_2$	DCE	90	75
12	$Cu(OTf)_2$	DCE	100	71
13[c]	$Cu(OTf)_2$	DCE	90	76
14[d]	$Cu(OTf)_2$	DCE	90	54
15[e]	$Cu(OTf)_2$	DCE	90	81
16[f]	**$Cu(OTf)_2$**	**DCE**	**90**	**91**

[a]Conditions: **1a** (0.30 mmol), **2a** (1.20 mmol), catalyst (30 mol %), solvent (2 mL), 48 h, under Ar. [b]Isolated yield. [c]Using 50 mol % of $Cu(OTf)_2$. [d]Using 20 mol % of $Cu(OTf)_2$. [e]Solvent (1 mL). [f]Using **1a** (0.60 mmol), **2a** (2.40 mmol), $Cu(OTf)_2$ (0.18 mmol), solvent (1 mL).

delight, **1a** could react with **2a** to give the desired product **3a** in 62% yield in the presence of $Cu(OTf)_2$ (30 mol %) in DCE (2 mL) at 80 °C for 48 h under an argon atmosphere (entry 1). Encouraged by this result, other catalysts were further examined, and we found they were either poorly effective ($Fe(OTf)_3$, $CuCl_2$, CuCl, and TfOH; entries 2−5) or entirely ineffective ($Zn(OTf)_2$; entry 6). To advance the process further, a subsequent survey on the role of various solvents for the aforementioned transformation revealed that DCE is the most suitable solvent, and other solvents such as CH_3CN, THF, CH_2Cl_2, and PhCl were less effective (entries 7−10). Note that increasing the temperature to 90 °C could improve the product yield up to 75%, but further enhancing the reaction temperature to 100 °C led to the yield reduction (entries 11−12). Subsequently, the loading of $Cu(OTf)_2$ was also investigated, yet 20 and 50 mol % of $Cu(OTf)_2$ did not significantly promote this reaction (entries 13 and 14). Interestingly, reducing the solvent to 1 mL could improve the yield to 81% (entry 15). Gratifyingly, in the presence of $Cu(OTf)_2$ (30 mol %) in DCE (1 mL) at 90 °C for 48 h, increasing the loading of **1a** and **2a** to 0.6 and 2.4 mmol, respectively, gave rise to an excellent yield of 91% (entry 16).

With the optimized conditions in hand (footnote a, Table 2), we then investigated the cross-coupling of various propargylic diols with diphenylphosphine oxide **2a** to explore the generality of this methodology, and the results were summarized in Table 2. First, various cycloalkyl-containing propargylic diols were examined, and the substrate **1b** carrying a cyclobutyl substituent could react with **2a** to afford the corresponding product **3b** in 65% yield (entry 2). However, a cyclopentyl-containing substrate **1c** provided two isomers **3c** and **3c′**, probably due to the occurrence of a 1,3-H shift during the catalyst process leading to the formation of **3c′** (entry 3). Interestingly, the substrate **1d** having a bulky cyclohexyl gave no trace of 1,3-butadiene product **3d**, but generated **3d′** in a moderate yield of 52% owing to the effect of steric hindrance (entry 4). It is worth noting that when using various diol precursors bearing one or two secondary racemic propargylic alcohols (**1e−1q**), high selectivity for the *E* stereoisomers of the products 2,3-bis(diarylphosphinyl)-1,3-butadienes (**3e−3q**) was observed because of steric hindrance, and the corresponding trace *Z* stereoisomers were not separated by column chromatography on silica gel. The result revealed that this novel coupling might undergo an S_N1-type reaction mechanism. As shown in Table 2, various propargylic diols (**1f−1n**) having different electron-withdrawing substituents such as chloro, bromo, iodo, cyano and trifluoromethyl on the phenyls were all efficiently reacted with **2a** via dehydrate cross-coupling reactions to give the major (*E*)-2,3-bis(diarylphosphinyl)-1,3-butadiene products (**3f−3n**) in moderate to good yields with the stereoselectivity for *E*-isomers determined by the coupling constant between the P atom and the C atom of benzene linked to double bonds on the basis of ^{13}C and ^{1}H NMR spectroscopic analysis.[6,10] However, propargylic diols bearing electron-donating substituents including methyl, alkoxyl, and mercapto on the benzene ring provided none of the expected 1,3-butadiene products, indicating that the electronic effect is evident in this transformation. Notably, the propargylic diol moiety showed a higher chemoselectivity over the chloro, bromo, and iodo atoms as leaving groups under the present conditions and 1,3-butadiene products (**3f−3h**) could be obtained by this coupling, which demonstrated the potential of this new approach for the construction of more complex molecules through the next coupling of these halide products. The bulky substrates containing a naphthyl moiety (**1o**) and a *tert*-butyl group (**1q**) could all undergo the coupling to produce the desired products (**3o** and **3p**). The heterocyclic propargylic diols having a thiophene ring (**1r** and **1s**) were also compatible with the present reaction conditions, affording the desired products **3r** and **3s** as a mixture of *Z*/*E* isomers in good total yields. In addition, 1-cyclohexyl-4-methylpent-2-yne-1,4-diol **1t** only gave **3t′** determined by ^{1}H and ^{13}C NMR spectroscopic analysis in 67% yield and the expected 1,3-butadiene product was not observed. Fortunately, the product **3a** was recrystallized from ethyl acetate/*n*-hexane as colorless crystals, and the molecular structure of **3a** was confirmed by X-ray diffraction analysis (CCDC 1873031).[11] The result clearly revealed that the phosphoryl moiety was preferentially installed at the C2- and C3-positions of **1a** in this coupling reaction.

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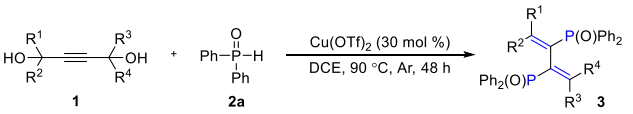
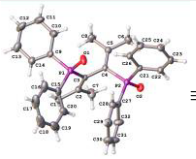
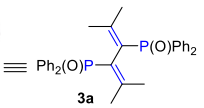
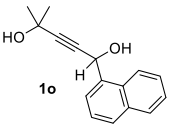
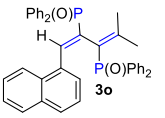
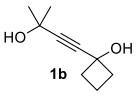
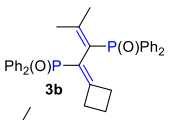
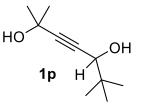
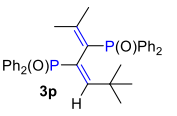
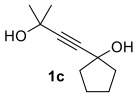
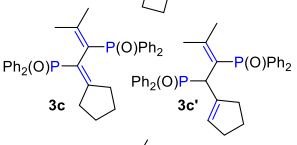
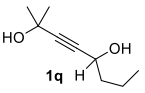
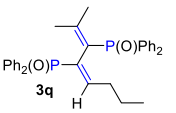
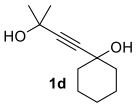
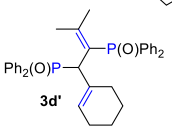
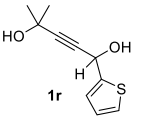
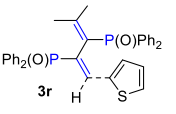
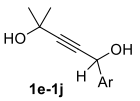
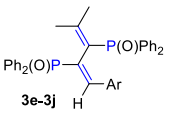
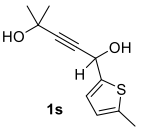
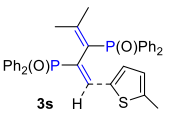
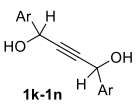
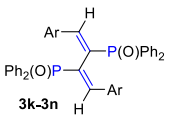
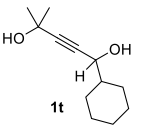
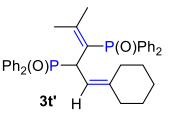
Table 2. Direct Twofold Cross-Coupling of Propargylic Diols with Diphenylphosphine Oxide[a]

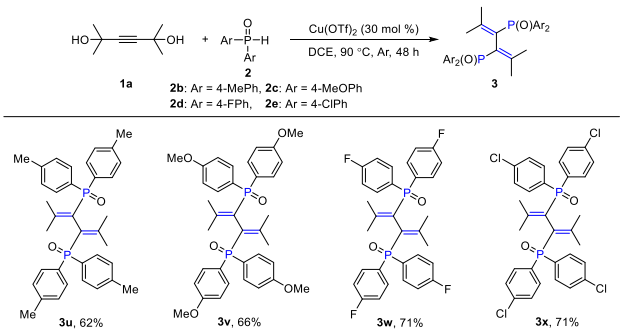


entry	propargylic diols **1**	product **3**	yield (%)[b]	entry	propargylic diols **1**	product **3**	yield (%)[b]
1		 **3a**	91	7	 **1o**	 **3o**	70
2	 **1b**	 **3b**	65	8	 **1p**	 **3p**	47
3	 **1c**	 **3c** **3c'**	86 (1:1.04)[c]	9	 **1q**	 **3q**	57
4	 **1d**	 **3d'**	57	10	 **1r**	 **3r**	62 (1.56:1)[d]
5	 **1e-1j**	 **3e-3j**	**3e**, Ar = C_6H_5, 62 **3f**, Ar = 4-ClC_6H_4, 62 **3g**, Ar = 4-BrC_6H_4, 60 **3h**, Ar = 4-IC_6H_4, 68 **3i**, Ar = 4-CNC_6H_4, 55 **3j**, Ar = 4-$CF_3C_6H_4$, 47	11	 **1s**	 **3s**	66 (1.70:1)[d]
6	 **1k-1n**	 **3k-3n**	**3k**, Ar = C_6H_5, 70 **3l**, Ar = 4-ClC_6H_4, 59 **3m**, Ar = 4-BrC_6H_4, 58 **3n**, Ar = 3-ClC_6H_4, 51	12	 **1t**	 **3t'**	67

[a]Reaction conditions: **1** (0.60 mmol), **2** (2.40 mmol), and $Cu(OTf)_2$ (0.18 mmol) in DCE at 90 °C for 48 h under argon. [b]Isolated yield. [c]The ratio of **3c**/**3c′** was determined by the isolated yield. [d]*E*/*Z* ratio was obtained by ^{31}P NMR spectroscopic analysis.

To further extend the scope of this reaction, some other *H*-phosphine oxides were also evaluated. As demonstrated in Scheme 2, apart from **2a**, other *H*-phosphine oxides such as **2b**, **2c**, **2d**, and **2e** were all suitable coupling partners, and the corresponding products (**3u**−**3x**) were generated in 62%, 66%, 71%, and 71% yields, respectively.

Scheme 2. Direct Twofold Cross-Coupling of 1a with *H*-Phosphine Oxides[a]



[a]Reaction conditions: **1a** (0.60 mmol), **2** (2.40 mmol), and $Cu(OTf)_2$ (0.18 mmol) in DCE at 90 °C for 48 h under argon. Isolated yield.

Notably, we found that the propargylic diol **1u** bearing a diphenyl group only gave a trace of the desired 1,3-butadiene product **3y** under the standard conditions, but it could react with **2a** to generate the major product **4a** containing a *β*-ketophosphine oxide framework, which is of interest for the application in the well-known HWE (Horner−Wadsworth−Emmons) reaction[12] and also exhibits wide-ranging biological activities[13] and eminent metal-complexing abilities.[14]

Similarly, the substrate **1v** could also afford the *β*-ketophosphine oxide **4b** in 43% yield along with the generation of the 1,3-butadiene product **3z** in 40% yield (Scheme 3). The results indicated that the formation of *β*-ketophosphine oxide might be attributed to the attack of H_2O onto the key allenic intermediate during the reaction process.

It is noteworthy that a gram-scale experiment was conducted by employing **1a** (15 mmol, 2.13 g) with **2a** (60 mmol, 12.12 g) under the optimal reaction conditions. The desired product **3a** was obtained in a high yield of 82%, showing that the present method could be easily adopted for the large-scale synthesis with high efficiency (Scheme 4).

Based on the above results and previous reports,[15] a plausible mechanism for the 2-fold cross-coupling is presented in Scheme 5. First, intermediate **A** was formed by the coordination of a copper cation to the triple bond and OH group. Next, the critical propargylic carbocation intermediate **B** could be easily gained through the elimination of the OH

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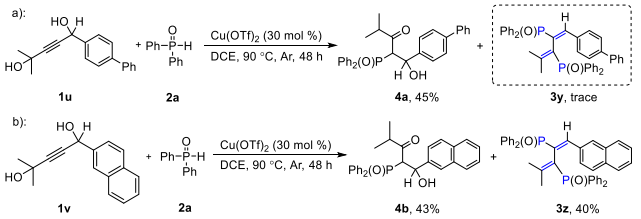
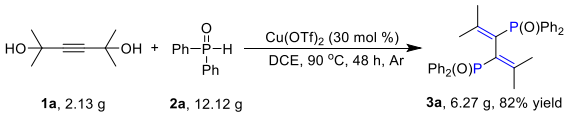
Scheme 3. 1u and 1v Reacted with 2a To Afford *β*-Ketophosphine Oxides

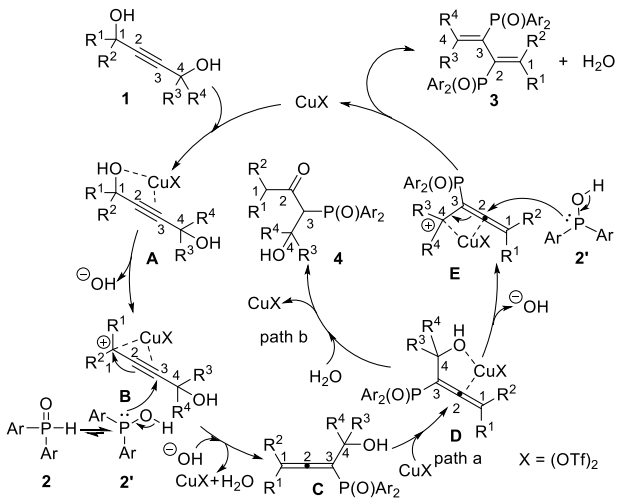


[a]Reaction conditions: **1a** (0.60 mmol), **2a** (2.40 mmol), and $Cu(OTf)_2$ (0.18 mmol) in DCE at 90 °C for 48 h under argon. Isolated yield.

Scheme 4. Gram-Scale Preparation of 3a



Scheme 5. Possible Mechanism for the Twofold Cross-Coupling Reaction



group with the assistance of a Lewis acid, $Cu(OTf)_2$.[15a−c] Then, in view of the least sterically hindered possibility, the nucleophile **2** (in the form of the trivalent phosphine oxide **2′**) attacked the C3-position of **B** via an S_N1-type substitution to provide the key product **C** of the first cross-coupling cycle. Subsequently, the second cross-coupling proceeded by a similar coordination of $Cu(OTf)_2$ to the allenyl and OH group, forming intermediate **D**,[15d] followed by the removal of the OH group to produce intermediate **E**. Finally, nucleophilic substitution of **2** onto the least sterically demanding C2-position of **E** afforded the desired product **3** along with the regeneration of $Cu(OTf)_2$ as a catalytically active species (path a). However, using some propargylic diols bearing bulky electron-donating substituents on the benzene ring of C4-position of **1** as substrates, the nucleophile H_2O instead of bulky **2′** attacked the C2-position of **D** (path b), resulting in the generation of *β*-ketophosphine oxide **4** owing to the effect of the steric hindrance.

In summary, we have developed the first efficient and practical Cu-catalyzed direct twofold C−P cross-coupling of various unprotected propargylic diols with *H*-phosphine oxides via an S_N1-type reaction, which provides a rapid strategy for a structurally diverse array of more highly substituted 2,3-bis(diarylphosphinyl)-1,3-butadiene compounds along with the construction of two new P−C_{sp^2} and two new C=C bonds. Importantly, this novel twofold cross-coupling could facilitate the creation of unique phosphorus-containing 1,3-buta-diene molecules bearing P−C−C−P backbones, which might further transform to a new type of more useful diphosphine ligands by ready reduction. Most attractively, the coupling reaction only uses inexpensive and commercially available $Cu(OTf)_2$ as the catalyst without the need for a base and a ligand, and various special 2,3-bis(diphenylphosphinyl)-1,3-butadienes could be conveniently obtained in a simple one-step process, which represents a prominent advantage of this method. In addition, the use of easily accessible propargylic diols prepared from a broad range of aldehydes and ketones, producing water as the only byproduct in this transformation, the operational simplicity, and the high step and atom economy mean this strategy will find widespread application in the preparation of important 2,3-bis(diarylphosphinyl)-1,3-butadiene frameworks in modern organic synthesis and coordination chemistry. Further mechanistic investigations and application research are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03985.

General experimental procedures, characterization data of all products (PDF)

Accession Codes

CCDC 1873031 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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