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Diverse C–P Cross-Couplings of Arylsulfonium Salts with Diarylphosphines via Selective C–S Bond Cleavage

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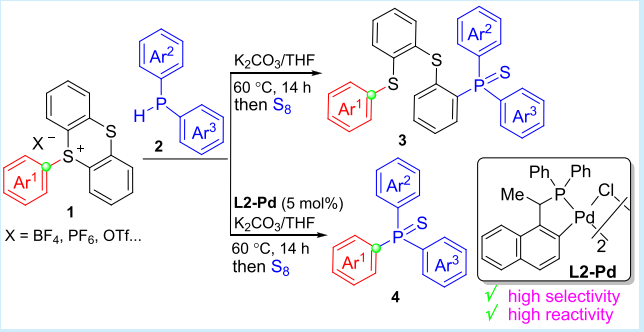
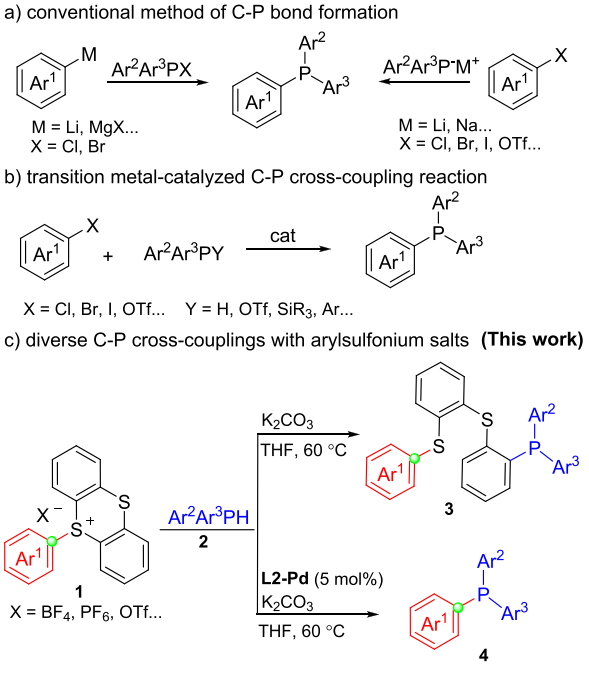
ABSTRACT: Diverse C–P cross-couplings of arylthianthrenium salts with diarylphosphines producing various triarylphosphines via highly selective C–S bond cleavage are reported. In the absence of catalyst, the reaction of arylthianthrenium salts with diarylphosphines undergoes phosphinative ring opening exclusively via the cleavage of an endocyclic C–S bond of a thianthrene skeleton. The use of a palladacycle catalyst under otherwise the same conditions enables the phosphination via the cleavage of an exocyclic C–S bond with significantly higher speed.



Triarylphosphines ($Ar^1Ar^2Ar^3P$) and their derivatives are well-known for their high utility in synthetic chemistry and catalysis,[1] biomedicines,[2] and materials science.[3] They are conventionally synthesized by either addition of a Grignard/organolithium reagent to a phosphine halide or reaction of a phosphide anion with an electrophile (Scheme 1a).[4] This method is intolerant to a wide variety of functional groups due to the harsh conditions. Alternatively, they can be prepared by transition-metal-catalyzed cross-coupling reaction of aryl-(pseudo)halides (Scheme 1b).[5] Although the compatibility is improved greatly by this method, special functional groups such as (pseudo)halides must be preinstalled on the starting materials. Indirect synthesis of triarylphosphines using phosphine oxides, phosphine boranes, or phosphonates, etc., have also been well documented;[6] however, the tedious protection/deprotection, or reduction, involving multiple steps is unavoidable. It is strongly desirable to develop direct and greener approaches to introduce phosphino groups onto the desired skeleton in a controlled manner. Herein, we report a new approach for highly selective installation of diarylphosphino groups onto (hetero)arenes yielding various triarylphosphines via diverse C–P cross-couplings of diarylphosphines with arylthianthrenium salts which can be readily prepared by site-selective aromatic C–H thianthrenation (Scheme 1c).

Sulfonium salts have been attracting increasing attention owing to their broad applications in synthetic chemistry.[7] Recently, arylsulfonium salts such as aryl-tetrafluorothianthrenium (Ar-TFT) salts, arylthianthrenium (Ar-TT) salts, and aryldibenzothiophenium (Ar-DBT) salts have been developed as a class of versatile electrophile reagents for various transformations by Ritter[8] and others.[9] An example of Michaelis–Arbuzov phosphonate synthesis using an Ar-TFT

Scheme 1. Strategies for Direct Synthesis of Triarylphosphines



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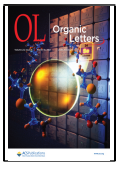

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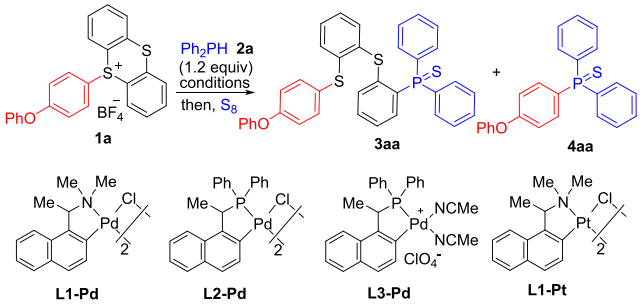
salt with triphenylphosphite ($P(OPh)_3$) under photoredox catalysis has been reported;[8a] however, the reaction of any arylsulfonium salts with diarylphosphines (Ar^1Ar^2PH) is unprecedented to the best of our knowledge. We have made continuous efforts[10] to develop new methods for construction of chiral phosphines by hydrophosphination of electron-deficient olefins.[11] We envisaged that triarylphosphines can be accessed by the reaction of arylsulfonium salts with diarylphosphines.

We began our investigation with the reaction of readily accessible sulfonium salt **1a** with Ph_2PH (**2a**). In the presence of a base, the reaction underwent phosphinative ring opening exclusively (Table 1, entries 1−2). The use of K_2CO_3 leads to

Table 1. Optimization of Conditions[a]



entry	catalyst[b]	base	solvent	yield (%)[c] 3aa	4aa
1	none	Cs_2CO_3	THF	86	0
2	none	KOH	THF	96	0
3	**none**	**K_2CO_3**	**THF**	99(99)	**0**
4	CuCl	K_2CO_3	THF	54	−
5	$Ni(cod)_2$	K_2CO_3	THF	68	0
6	$Pd(OAc)_2$	K_2CO_3	THF	4	21
7	$Pd_2(dba)_3$	K_2CO_3	THF	5	65
8	$Pd(PPh_3)_4$	K_2CO_3	THF	15	85
9	$Pd(OAc)_2$/binap	K_2CO_3	THF	6	94
10	$Pd(OAc)_2$/segphos	K_2CO_3	THF	8	90
11	**L1-Pd**	K_2CO_3	THF	33	67
12	**L2-Pd**	**K_2CO_3**	**THF**	**4**	96(95)
13[d]	**L2-Pd**	K_2CO_3	THF	2	89
14	**L3-Pd**	K_2CO_3	THF	7	85
15	**L1-Pt**	K_2CO_3	THF	97	0
16	**L2-Pd**	K_2CO_3	dioxane	6	94
17	**L2-Pd**	K_2CO_3	MTBE	4	12
18	**L2-Pd**	K_2CO_3	toluene	3	4

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.14 mmol), base (3.0 equiv), solvent (2 mL), at 60 °C for 14 h. [b]Catalyst (5 mol % of M) was loaded if applicable. [c]The yields were obtained by ^{31}P NMR analysis of the crude reaction mixture after quenching with sulfur using $(PhO)_3P(O)$ as an internal standard. Isolated yields in parentheses. [d]The reaction was quenched after 1 h. THF = tetrahydrofuran; MTBE = methyl *tert*-butyl ether.

product **3aa**[12] in a quantitative yield (entry 3). The X-ray analysis of **3aa** (CCDC-2025189) unambiguously confirmed its structure. Next, a few transition metal catalysts were examined (entries 4−8), and it was found that $Pd(OAc)_2$ can inhibit the ring-opening product **3aa** significantly and yield another cross-coupling product **4aa** in 21% yield. Further screening revealed that the chelation ligands (binap, segphos) can improve its yield greatly (entries 9−10). The best yield of **4aa** (95%) with high selectivity (**3aa**/**4aa** = 4/96) was achieved by employing the *C,P*-palladacycle **L2-Pd** as the catalyst under the given conditions (14 h), with thianthrene (TT) being recovered in 90% yield (entry 12). When the reaction time was shortened to 1 h, **4aa** was formed in 89% yield accompanied by 2% of **3aa** (entry 13). The *C,N*-palladacycle **L1-Pd** did not give satisfactory selectivity (entry 11). The cationic analogue **L3-Pd** can also work producing **4aa** in a slightly lower yield. The use of the platinum analogue **L1-Pt** did not give **4aa** at all.[13] Screening of solvents evidenced that dioxane can give similar results as THF, while MTBE and toluene are not the appropriate ones. Several other types of arylsulfonium salts including **1a**[2]−**1a**[5] were also examined indicating that only the Ar-TT salt can undergo the divers C−P cross-couplings in a highly selective manner.

The high selectivity of **3aa**/**4aa** (4/96) is attributed to the high catalytic activity of **L2-Pd** which produces **4aa** with significantly higher speed than the formation of **3aa**. Control experiments for conversion versus time curves for the reaction of **1a** and **2a** were performed (Figure 1). Under the catalytic

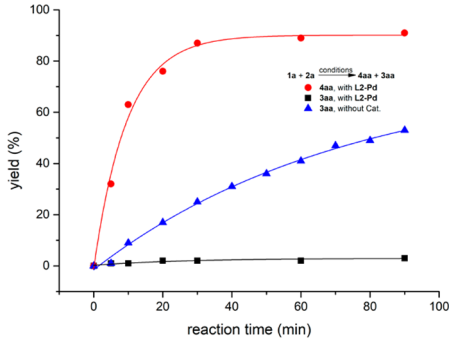


Figure 1. Profiles for the reaction of **1a** and **2a**.

conditions, the production of **4aa** catalyzed by **L2-Pd** is about 24 times faster than that of **3aa**. For 50% conversion of **1a**, it takes only about 7 min with **L2-Pd** compared to around 80 min without the catalyst.

Under the optimized conditions for the phosphinative ring opening, we assessed the scope of Ar-TT salts with Ph_2PH, and the results were summarized in Scheme 2. A variety of *para*-, *meta*-, *ortho*-substituted Ar-TT salts successfully underwent phosphinative ring opening, tolerating a broad range of functional groups giving **3aa**−**3pa** in mild to excellent yields. Notably, this transformation exclusively gave the ring-opening product **3**, the formation of **4** being not observed. Ring openings of cyclic sulfonium salts by a nucleophile[8j,14] (ArSNa, ArONa, $NaBAr_4$, NMe_4F) have been reported; however, high selectivity remains a challenge for the ring opening.

Next, the scope of Ar-TT salts and diarylphosphines for the **L2-Pd**-catalyzed phosphination under the optimized conditions was investigated (Scheme 3). A variety of *para*-, *meta*-, *ortho*-substituted Ar-TT salts were successfully coupled to give products **4aa**−**4ya** in generally good to excellent yields, tolerating a wide range of functional groups such as ethers, esters, amines, amides, halogens, olefins, alcohols, heterocycles, etc. The presence of sensitive functionalities such as Br (**1b**), OTf (**1g**), and OH (**4ta**) did not hamper the reaction; however, I (**1f**) cannot be well tolerated and can give the double phosphination product.[15] Thianthrenation takes place at the 2-position on the thiophene ring forming 2-thienyl-thianthrenium salts (**1u**−**1w**) which can react smoothly with Ph_2PH to give the phosphination products (**4ua**−**4wa**), while

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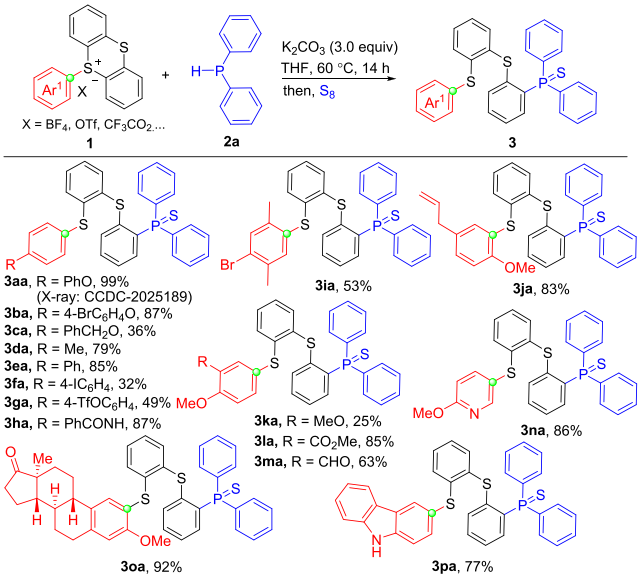
Scheme 2. Phosphinative Ring Opening of Ar-TT Salts with Ph_2PH[a]



[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.14 mmol), K_2CO_3 (3.0 equiv), THF (2 mL), at 60 °C for 14 h. Isolated yield of sulfide **3** after quenching of the reaction with sulfur.

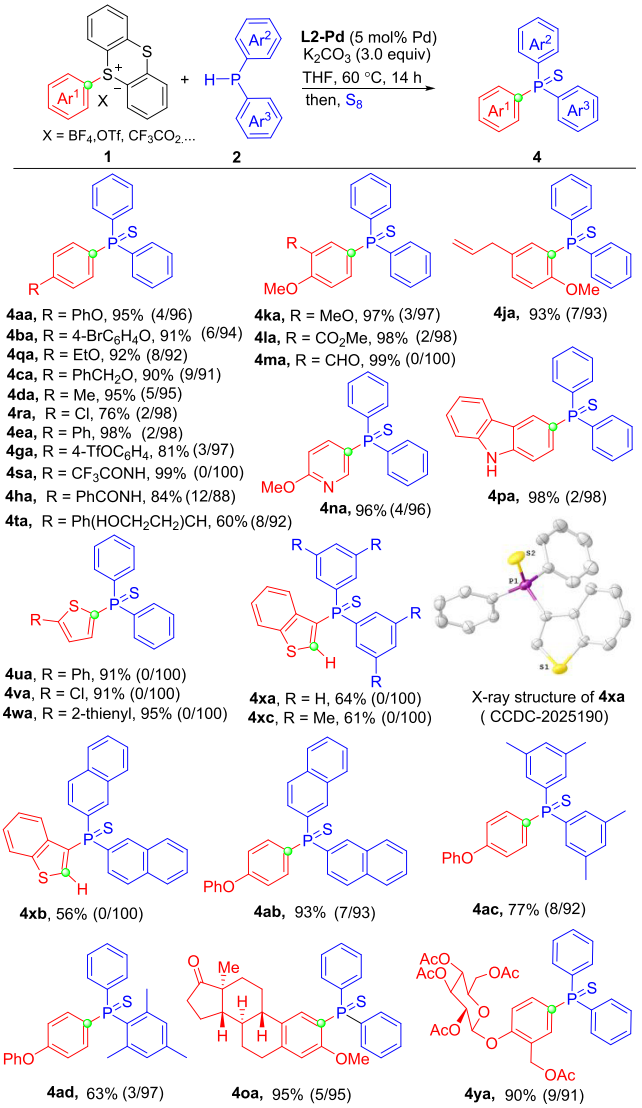
it takes place at the 3-position on the benzothiophene ring to give **1x** which can react with diarylphosphines to give products **4xa**−**4xc**. The X-ray analysis of **1x** (CCDC-2057925) and **4xa** (CCDC-2025190) unambiguously confirmed their structures.[15] This protocol can be used to manipulate the complex, biologically relevant scaffold derived from estrone (**4oa**, 95%) and salicin pentaacetate (**4ya**, 90%) via selective incorporation of a diphenylphosphino group. In addition, substituted diarylphosphino groups can be efficiently installed (**4ab**, **4xb**, **4ac**). Unsymmetrical diarylphosphine Ph(Mes)PH (**2d**) can be also coupled to give **4ad** in 63% yield. Optically pure (*S*)-**L2-Pd** as a chiral catalyst was investigated for this transformation. Unfortunately, no ee (ee% = 0) was observed under the conditions.

To gain insights into the reaction mechanism, radical trapping experiments using TEMPO or BHT as the scavenger were performed, and the results indicated that an aryl radical intermediate is not formed during the reaction (Scheme 4a). The reaction of sterically hindered Mes-TT salt (**1z**) with Ph_2PH only gives the ring-opening product **3za** (Scheme 4b). The congestion from the mesityl group inhibits the formation of **4za** completely even with the **L2-Pd**. When sterically more hindered $(Mes)_2PH$ was used instead of Ph_2PH, no reaction takes place at all.

Tertiary triarylphosphine products can be obtained without sulfurization under the standard conditions. An example (eq 1) was shown to prepare **5aa** (90% isolated yield). Slight oxidation was observed during the isolation of the product if not protected. To demonstrate the scalability of this protocol, 1.20 g of salicin pentaacetate (pharmaceutical) was used for the synthesis of **4ya** with **L2-Pd** (2 mol % Pd). The target product **4ya** was isolated in 85% overall yield (two steps), and thianthrene (**TT**) was recovered in 91% overall yield (eq 2).

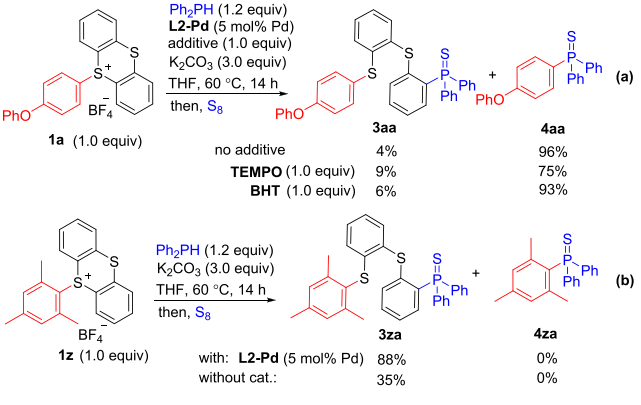
In summary, we have disclosed a new approach for the synthesis of various triarylphosphines via diverse C−P cross-couplings of arylthianthrenium salts with diarylphosphines.

Scheme 3. Palladium-Catalyzed Phosphination of Ar-TT Salts with Diarylphosphines[a]



[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.14 mmol), **L2-Pd** (5 mol % of Pd), base (3.0 equiv), THF (2 mL), at 60 °C for 14 h. Isolated yield of sulfide **4** after quenching of the reaction with sulfur. The ratio of the corresponding **3**/**4** determined by ^{31}P NMR analysis of the crude reaction mixture is indicated in parentheses.

Scheme 4. Control Experiments



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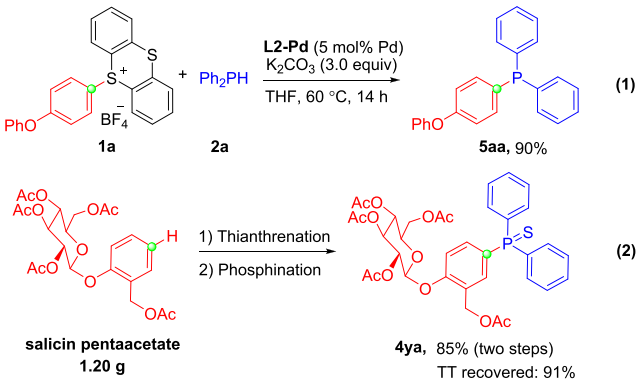

The use of a palladacycle **L2-Pd** as a catalyst enables the C−P cross-coupling via cleavage of an exocyclic C−S bond with significantly higher speed than that via cleavage of an endocyclic C−S bond. This protocol provides an efficient way for highly selective installation of diarylphosphino groups onto a wide scope of arenes, heteroarenes, and complex molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00748.

Experimental details, characterization data including ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra, X-ray data (PDF)

Accession Codes

CCDC 2025189−2025190 and 2057925 contain 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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