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Ruthenium-Catalyzed Gram-Scale Preferential C−H Arylation of Tertiary Phosphine

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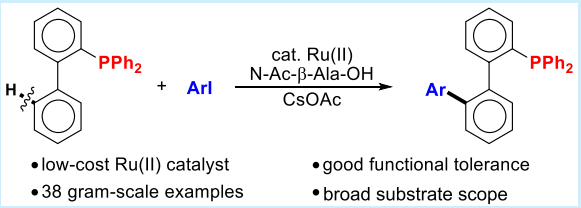
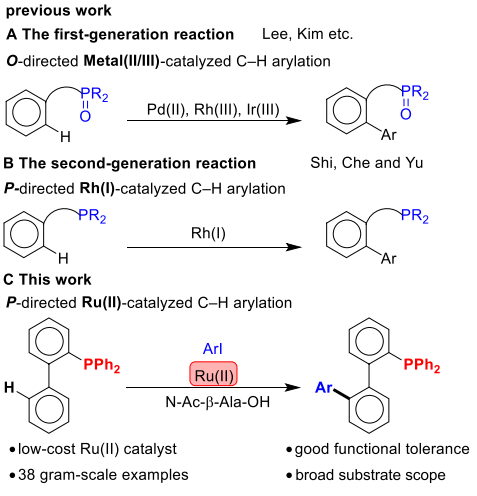
Supporting Information

ABSTRACT: A general protocol for site-preferential mono-C−H arylation of tertiary phosphine ligands catalyzed by a ruthenium(II) complex was devised. This protocol gives access to a series of modified Buchwald−biaryl monophosphines on a gram scale in moderate to excellent yields. A catalytic cycle is proposed derived from knowledge of the intermediates observed by ESI-MS. Importantly, these monoarylated products could be further transformed into dibenzophosphole derivatives.



C−H bond activation catalyzed by a coordination complex has been an important approach in organic synthesis.[1] The precise and rational design of the catalyst is extremely important for the sequence involving coordination, activation, and departure of the catalyst with the reaction substrate, which define the effectiveness of a catalytic reaction.[2] Therefore, it is a great challenge to choose a reasonable catalyst for a substrate with a strong coordinating group. Tertiary phosphines (PR_3) belong to a critically important cornerstone where they are widely used in transition-metal catalysis and functionalizing organic materials for their unique optical properties.[3] Moreover, their steric and electronic properties can be altered by varying the R groups.[4] For instance, Buchwald−biaryl monophosphines with a large steric hindrance have been widely used as supporting ligands in metal-catalyzed C−C, C−O, and C−N bond construction processes.[5] Consequently, efficient and diverse synthesis of PR_3 has been arguably the most important contributor to the advancement of the metal-catalysis field. In recent decades, transition-metal-catalyzed C−H bond activation strategy has provided a powerful tool for synthesis of PR_3, which has enabled more efficient chemical synthesis by avoiding the traditional requirement of preinstalled functional handles.[6,7] Among various modifications, arylation of PR_3 via C−H bond activation has received widespread interest. In this respect, Lee,[8] Kim,[9] and other groups[10] developed the first-generation arylation of phosphine oxides via C−H activation catalyzed by transition metals, such as Pd(II), Rh(III), and Ir(III) (Scheme 1A). However, an inevitable limitation for the first-generation method needs to utilize phosphine oxides as substrates, which increases additional synthetic steps for preoxidation of phosphines followed by reduction of the phosphine oxides. Therefore, a more efficient method for direct C−H arylation of PR_3 has been developed. Recently, Shi[11] and the group of Che and Yu[12] realized the second-generation *P*-atom-directed Rh(I)-catalyzed C−H arylation of PR_3 (Scheme 1B). Despite great success for atom- and step-economical transformations, the development of a new catalytic system for metal-catalyzed C−H arylation of PR_3 is

Scheme 1. Modification of Tertiary Phosphines via Metal-Catalyzed C−H Arylation



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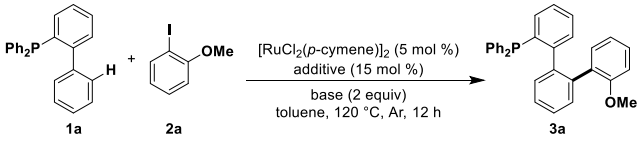
highly attractive and a great challenge due to their strong coordination and instability.[13]

Prompted by the inspiring work of amino acid promoted C−H activation[14] and Ru(II)-catalyzed C−H functionalizations by Ackermann[15] and other groups[16] and following a study on the direct functionalization of inert C−H bonds,[17] coordination-directed tandem reaction,[18] and assembly process mechanism,[19] we herein describe a general and efficient method for gram-scale synthesis of modified Buchwald−biaryl phosphine ligands by Ru(II)-catalyzed preferential mono-C−H arylation of PR_3 assisted by monoprotected amino acid ligands (Scheme 1C).

Initially, we selected readily available [1,1′-biphenyl]-2-yldiphenylphosphane (**1a**) with 2-iodoanisole (**2a**) as a model reaction (Table 1; for more details, see the Supporting Information). The reaction gave the desired arylation product in 46% yield in the presence of 5 mol % of $[RuCl_2(p\text{-cymene})]_2$, 15 mol % of 1-AdCOOH, and 2 equiv of CsOAc at 120 °C under argon in toluene (entry 2). No product was detected in the absence of additive or base (entry 1, 3), indicating that both play important roles in this transformation. Then a series of ligands were screened (entry 4−11), and an improved catalytic efficacy proved viable for N-Ac-β-Ala-OH (entry 11). Finally, we tentatively increased the concentration of the PR_3, and as we expected, a higher yield of **3a** up to 95% was obtained (entry 12).

Table 1. Reaction Conditions Screening[a]



1a 2a 3a

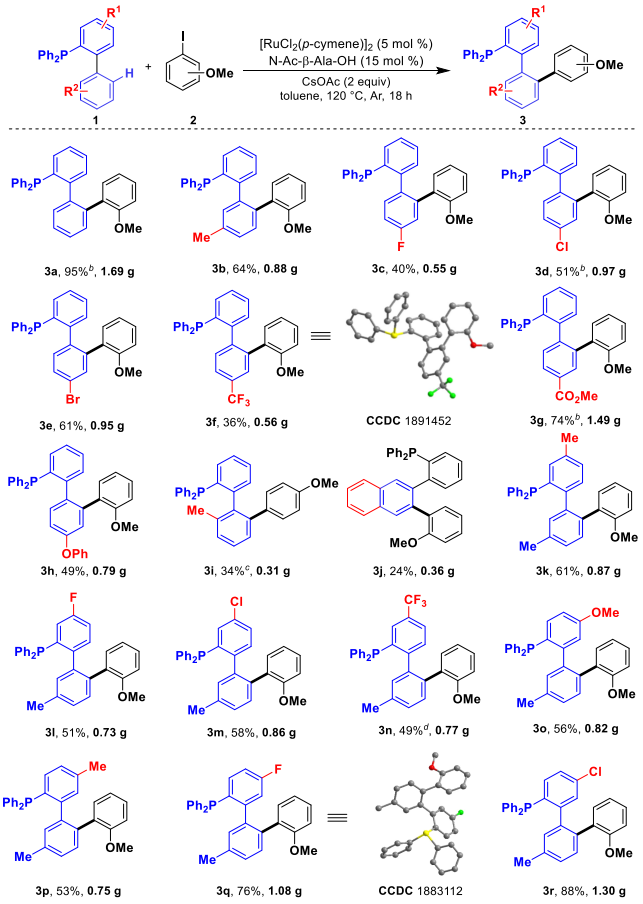
entry	additive	base	yield of **3a** (%)
1	1-AdCOOH		nd
2	1-AdCOOH	CsOAc	46
3		CsOAc	nd
4	PivOH	CsOAc	47
5	$MesCO_2H$	CsOAc	52
6	N-Boc-lle-OH	CsOAc	13
7	N-Ac-lle-OH	CsOAc	64
8	N-Ac-L-Val-OH	CsOAc	60
9	N-Ac-L-Phe-OH	CsOAc	61
10	N-Ac-L-Ala-OH	CsOAc	60
11	N-Ac-β-Ala-OH	CsOAc	69
12[b]	**N-Ac-β-Ala-OH**	**CsOAc**	**95 (1.69 g)**

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), additive (15 mol %), and CsOAc (0.2 mmol) in 1 mL of toluene at 120 °C under argon, 12 h, isolated yields. [b]**1** (4.0 mmol), **2** (6.0 mmol) in 2 mL of toluene, 120 °C, 18 h.

With the optimized reaction conditions in hand, we first explored its applicability for a range of tertiary phosphines (Scheme 2). Substrates with different substituents were tested, considering the conversion of substrates and the oxidation of the products during column chromatography separation process, and the results were as follows. As we expected, the reaction starting from diverse PPh_2-based ligands led to a series of *ortho*-arylated Buchwald−biaryl phosphines **3** on a gram scale. A wide scope of functional groups, such as Me (**1b**), F (**1c**), CF_3 (**1f**), CO_2Me (**1g**), PhO (**1h**), and naphthyl (**1j**), were explored, affording the corresponding products in moderate yields (24−74% yields, 0.36−1.49 g). Importantly, even an active Cl− or Br− substituent could successfully survive under these conditions, giving the desired products on a large scale (**3d**, 51%, 0.97 g, and **3e**, 61%, 0.95 g), which could easily be further transformed. The *ortho*-substituent such as Me (**2i**) gave the corresponding arylated product in 34% yield (0.31 g), indicating a pronounced steric effect on the reaction. Moreover, aryl groups attached to phosphine-bearing electron-donating and electron-withdrawing substituents, such as Me (**1k**, **1p**), OMe (**1o**), F (**1l**, **1q**), Cl (**1m**, **1r**), and CF_3 (**1n**), gave the corresponding products in moderate to excellent yields on a large scale (49−88% yields, 0.73−1.30 g). Notably, trace biarylated product was detected in the reaction system because the selectivity of this catalytic system was excellent. The structures of **3d**, **3f**, **3i**, **3k**, and **3q** were determined from single-crystal X-ray diffraction.

We next explored the scope of aryl iodides (Scheme 3). To our delight, substrates of aryl iodides bearing electron-donating substituents on the aryl rings, such as OMe (**2d**, **2f**), Me (**2e**, **2g**), NMe_2 (**2i**), and 3,4-methylenedioxyl (**2p**), gave the corresponding products in reasonable yields (67−76% yields, 1.15−1.37 g). Aryl groups bearing electron-withdrawing groups (CO_2Me, CN, COMe) also led to the desired products (**4c**, **4j**, **4l**, **4m**) on a gram scale (30−65% yields, 0.53−1.22 g).

Scheme 2. Scope of Substituted Triarylphosphines[a]



[a]Reaction conditions: **1** (3.0 mmol), **2** (4.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), N-Ac-β-Ala-OH (15 mol %) and CsOAc (6.0 mmol) in 2 mL of toluene at 120 °C under argon, 18 h, isolated yields. [b]**1** (4.0 mmol), **2** (6.0 mmol) in 2 mL of toluene, 120 °C, 18 h. [c]**1** (2.0 mmol), **2** (3.0 mmol) in 1 mL of toluene, 120 °C, 16 h. [d]Reaction conducted at 140 °C.

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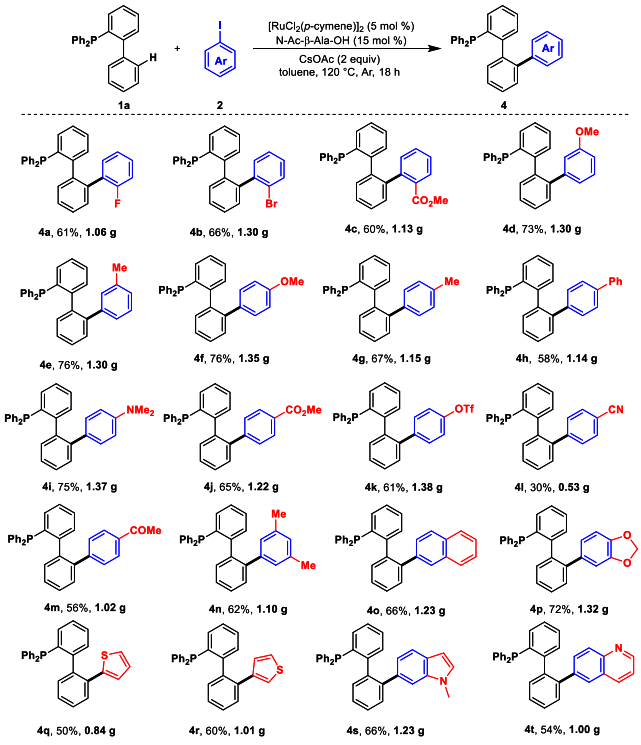
Scheme 3. Scope of Aryl Iodides[a]



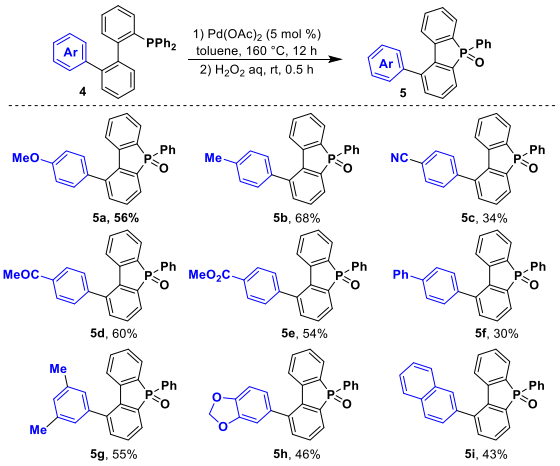
[a]Reaction conditions: **1a** (4.0 mmol), **2** (6.0 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), N-Ac-*β*-Ala-OH (15 mol %), and CsOAc (8.0 mmol) in 2 mL of toluene at 120 °C under argon, 18 h. Isolated yields.

Excitingly, the Br− and OTf− substituents on aryl iodides gave the corresponding arylated products in moderate yields (**4b**, 66%, 1.30 g, and **4k**, 61%, 1.38 g). Dimethyl-substituted aryl iodide was efficiently coupled and furnished the product **4n** in 62% yield (1.10 g). Additionally, benzene- and naphthalene-containing substrates were also found to be tolerable (**4h**, 58%, 1.14 g, and **4o**, 66%, 1.23 g). It is noteworthy that heteroaryl substrates with thiophene, indole, and quinoline efficiently coupled and furnished a series of heteroaryl monophosphines (**4q**−**t**) in moderate yields (50−66% yields, 0.84−1.23 g). In addition, the structures of **4b**, **4s**, and **4t** were confirmed by X-ray crystallographic analyses. Unfortunately, no product was observed when the P-atom was substituted with alkyls such as Cy and *t*-Bu or simple tertiary phosphines, referred to PPh_3.

Phospholes are widely used in organic materials for their excellent characteristic optical and electronic properties.[20] We further transformed these arylated tertiary phosphines into phosphole derivatives in a high-efficiency manner developed by Chatani,[21] and a series of phospholes derivatives bearing electron-donating (OMe, Me, and 3,4-methylenedioxyl) and electron-withdrawing groups (CN, COMe, and CO_2Me) were prepared in moderate yields (Scheme 4). Moreover, the benzene- and naphthalene-containing substrates were also found to be tolerable and gave the desired products in 30% (**5f**) and 43% (**5i**) yields, respectively. Additionally, exploration of their fluorescent properties is ongoing in our laboratory.

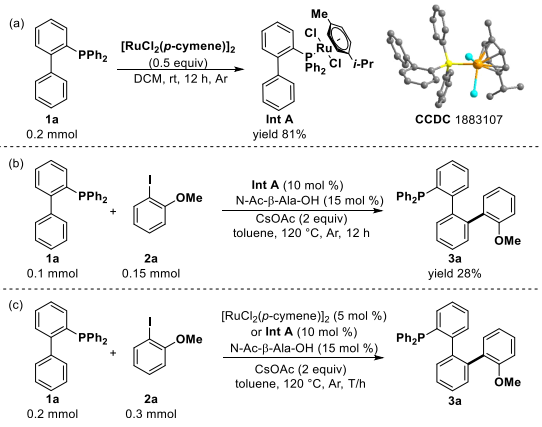
To gain insight into the reaction mechanism, an intermediate Ru(II) **Int A** was prepared and the structure of Ru(II) **Int A** was confirmed by X-ray crystallographic analysis (Scheme 5a). The arylation of **1a** under the optimal conditions was suppressed in the presence of 5.0 mol % of Ru(II) **Int A**,

Scheme 4. Scope of Phosphole Derivatives[a]



[a]Reaction conditions: **4** (0.3 mmol), $Pd(OAc)_2$ (5 mol %) in 1 mL of toluene at 160 °C under argon, 12 h, isolated yields.

Scheme 5. Control Experiments



and a 20% yield of arylated product was obtained, indicating that Ru(II) **Int A** may not be the active Ru(II) species (Scheme 5b). Additionally, time-dependent control experiments were conducted (Scheme 5c), and Ru(II) **Int A** showed lower catalytic activity over time (Figure 1). These results further confirmed that an active Ru(II) species, but not the Ru(II) **Int A**, might be generated in situ initially with the aid of MPAA and bases.

In order to provide information on the mechanism of this transformation, the control reactions of [1,1′-biphenyl]-2-

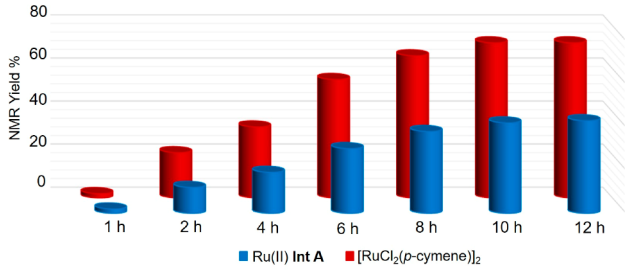


Figure 1. Yield profile for the reaction of **1a** with **2a** in the presence of $[RuCl_2(p\text{-cymene})]_2$ (5 mol %) and Ru(II) **Int A** (10 mol %), respectively. Each data point represents the average of three independent trials.

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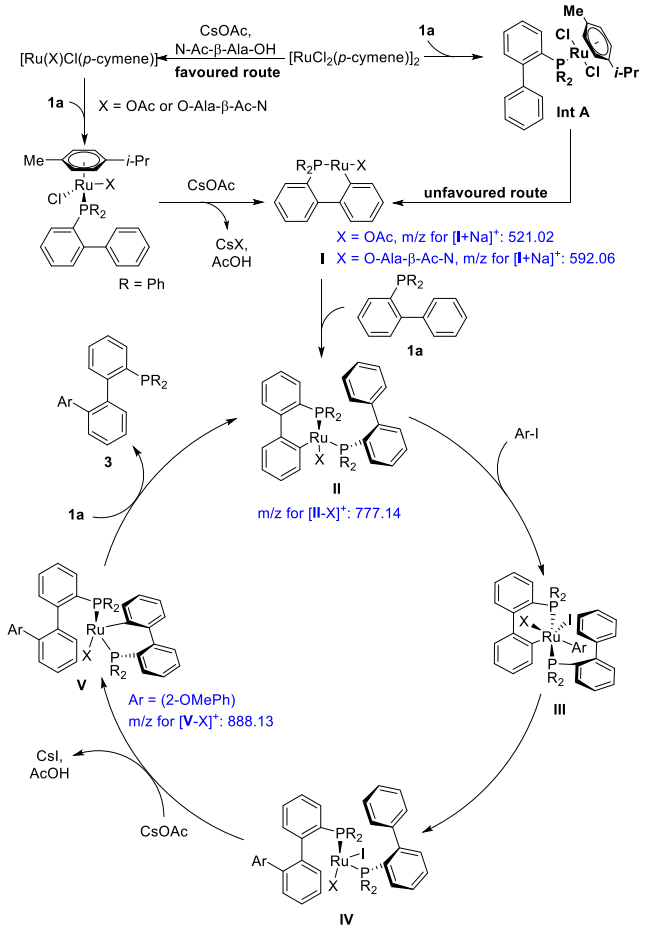
yldiphenylphosphane (**1a**) with 2-iodoanisole (**2a**) were monitored by ESI-MS.[12,22] These results indicate the activated intermediates **I**, **II**, and **V** involved in the catalytic process, consistent with the C−H bond activation by Ru(II) species (Figure S1; for details, see the Supporting Information).

On the basis of these experimental results and previous reports,[12,14e−g] a plausible process is proposed (Scheme 6). In

Scheme 6. Proposed Mechanism for the Catalytic Cycle



the absence of a Ru-N-Ac-*β*-Ala-O species and with the knowledge that both additives are required, we speculate that the CsOAc neutralizes the amino acid, which then coordinates with $[RuCl_2(p\text{-cymene})]_2$, thus generating the activated Ru(II) species (Figure S2; for details see the Supporting Information). Then the six-membered cyclometalated Ru(II) complex **I** (detected by ESI-MS) is formed via the *ortho*-ruthenation of **1a** with the activated Ru(II) species in the presence of base. Oxidative addition of aryl iodide to the thus-formed Ru(II) species **II** and formation of the complex **III**, followed by reductive elimination, intramolecular C−H bond activation (**V**, detected by ESI-MS), and coordination, releases the product **3** and regenerates the activated Ru(II) intermediate **II**.

In summary, we developed a general and efficient protocol for C−H arylation of tertiary phosphine catalyzed by ruthenium(II) complex. Its key rational design involves the coordination of an amino acid to the $[RuCl_2(p\text{-cymene})]_2$ that enables site-preferential functionalization of tertiary phosphines via *P*-atom-directed mono-C−H arylation, affording a series of Buchwald−biaryl phosphines with various functional groups, such as CN, Br, and OTf. Importantly, all of the monoarylation products were synthesized on gram scale, which could be further transformed into phosphole derivatives. Moreover, ESI-MS was used to elucidate the possible mechanism of the reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00888.

Detailed experimental procedures, compound characterization data (PDF)

Accession Codes

CCDC 1883107−1883108, 1883110−1883113, 1883116, and 1891452−1891453 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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