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Assembly of Indole Cores through a Palladium-Catalyzed Metathesis of Ar−X σ-Bonds

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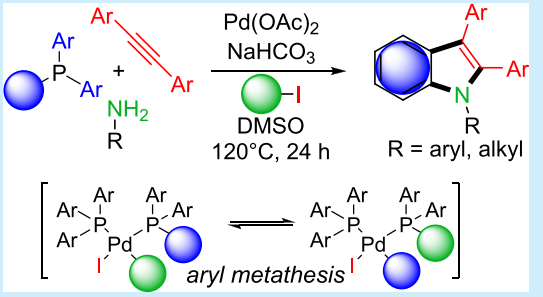
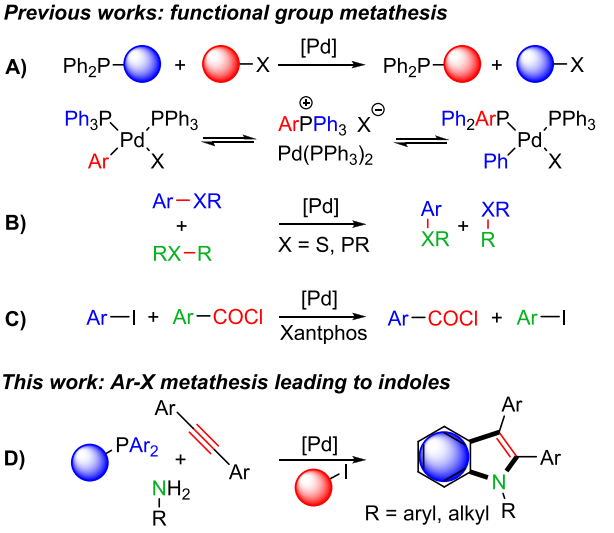
ABSTRACT: We describe the development of a new method for construction of highly substituted indole scaffolds through the strategic utilizing of the metathesis of Ar-X σ-bonds based on the dynamic nature of palladium-based oxidative addition/reductive elimination. A suitable and simple catalytic system has provided an appropriate platform for a productive ligand exchange and consecutive carbopalladation/C−H activation/amination of phosphine ligands with alkynes and aromatic/aliphatic amines for construction of structurally diverse indoles.



Phosphines play a crucial role in most transition-metal-catalyzed cross-coupling reactions in stabilizing the active metal center and fine-tuning the selectivity of the conversion.[1] The initially formed aryl palladium species, however, have been reported to frequently undergo an undesirable aryl/aryl interchange with the aryl substituents of triarylphosphine ligands via C−P bond scission, leading to undesired scrambled side products and deactivation of the catalyst.[2] Accordingly, early studies were focused on shutting down this side trail. However, by the accumulation of mechanistic data,[3] new avenues for developing various catalytic reactions through the strategic utilization of the metathesis of Pd−C and P−C bonds have been recently opened.[4] The catalytic redistribution of aryl groups between aryl electrophiles and aryl phosphines via reductive elimination of the phosphine ligand and the aryl group from the phosphine-ligated Pd^{II}−aryl complex to form the phosphonium intermediate has been developed into a useful synthetic transformation (Scheme 1A). In this regard, in 2017, Morandi et al. pioneered a Pd-catalyzed C−S or C−P bond metathesis via catalytic redistribution of aryl groups between aryl electrophiles and aryl sulfides and aryl phosphines (Scheme 1B).[5] Furthermore, the Morandi and Arndtsen research groups developed in parallel a functional group metathesis between iodoarenes and acid chlorides employing metathesis-active sterically encumbered Xantphos ligand to promote scrambling of the aryl groups on the aryl iodide and the aroyl chloride through reversible oxidative addition and carbonylation (Scheme 1C).[6] Obviously, creating a suitable catalytic system to provide an appropriate platform for a productive ligand exchange would find great applications in organic synthesis.

Inspired by recent advances in this area, we set out to identify reaction conditions to construct indole scaffolds with the benzoic ring built by the aryl section of simple triarylphosphines via the metathesis of Ar−X σ-bonds (Scheme 1D). Aryl's attachment to phosphorus can be activated via a controlled exchange between P−Ar and Pd−Ar, and it can

Scheme 1. Pd-Catalyzed Redistribution of Aryl Groups



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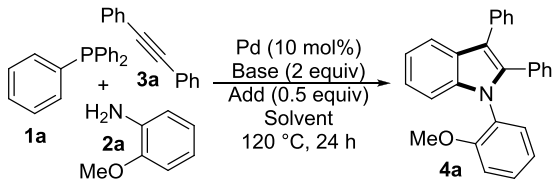
participate in a cascade annulation reaction for the purpose of the construction of more complex molecules, which is unprecedented to the best of our knowledge and would be very attractive. This transformation exploits palladium-catalyzed reversible oxidative addition/reductive elimination chemistry to offer the synthesis of a diverse array of highly functionalized indoles in high yields and opens a new window for the application of simple phosphines in the assembly of indole cores. Because indole rings are ubiquitous in natural products and pharmaceuticals[7] and are nominated as the fourth most dominant heteroaromatics,[8] a high-yielding general approach to their synthesis is highly desirable.[9]

The advancement of a controlled ligand exchange in a palladium-catalyzed carbopalladation/annulation/amination cascade for the construction of indole core, however, would encounter challenges via some probable side reactions. Classical Larock indole synthesis via the assembly of amines and alkynes,[9h] Buchwald−Hartwig amination of iodoarenes for the construction of diaryl amines,[10] and the assembly of alkyne and arenes for the construction of various carbocycles[11] are some competing paths in case. Suppressing the side oxidative addition of iodoarene to palladium(0) and the alkyne carbopalladation reaction is a further challenge.[12]

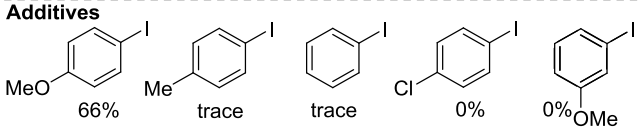
At the outset of our investigations, triphenylphosphine (**1a**), 2-methoxy aniline (**2a**), and diphenylacetylene (**3a**) were selected as the model substrates (Table 1). In general, it has been reported that Ar/Ar exchange between P−Ar and Pd−Ar usually becomes more realistic with electron-rich aryl groups, especially in polar solvents.[13] Accordingly, iodoanisole was added for C−P bond stimulation via phosphonium salt assembly. Among the palladium catalysts tested, $Pd(OAc)_2$ afforded the annulation product in a better yield of 48% (entries 1−3). Screening solvents showed that although solvents including ACN, chlorobenzene, THF, and toluene were undesirable compared with DMF, using DMSO improved the yield (entries 4−8). A screening of different bases revealed that switching the base to $NaHCO_3$ improved the yield (entry 12). No improved yield was obtained by varying the reactant equivalents. (See Table S2 in the Supporting Information for details.) The reaction was totally suppressed when $Pd(OAc)_2$ was removed. A control experiment also confirmed the crucial role of the iodoanisole as the additive. We probed if other iodoarenes may be more suited to favor the aryl scrambling process; however, no more improvements were achieved using various aryl iodides (Table 1). Eventually, we found that treating triphenylphosphine **1a** with 2-methoxy aniline **2a** (2 equiv), diphenylacetylene **3a** (1 equiv), iodoanisole (0.5 equiv), $NaHCO_3$ (2.0 equiv), and $Pd(OAc)_2$ (10 mol %) in DMSO (1 mL) led to the chemoselective assembly of indole **4a** in 66% isolated yield.

Table 1. Optimization of Reaction Conditions[a]



entry	Pd	base	solv	yield (%)[b]
1	$PdCl_2$	K_2CO_3	DMF	26
2	$Pd(OAc)_2$	K_2CO_3	DMF	48
3	$Pd(dba)_2$	K_2CO_3	DMF	35
4	$Pd(OAc)_2$	K_2CO_3	ACN	33
5	$Pd(OAc)_2$	K_2CO_3	DMSO	57
6	$Pd(OAc)_2$	K_2CO_3	PhCl	28
7	$Pd(OAc)_2$	K_2CO_3	THF	trace
8	$Pd(OAc)_2$	K_2CO_3	toluene	21
9	$Pd(OAc)_2$	Na_2CO_3	DMSO	55
10	$Pd(OAc)_2$	Cs_2CO_3	DMSO	49
11	$Pd(OAc)_2$	KOH	DMSO	trace
12	**$Pd(OAc)_2$**	**$NaHCO_3$**	**DMSO**	**66**

Additives



[a]Reaction conditions: phosphine **1a** (0.1 mmol), aniline **2a** (0.2 mmol), alkyne **3a** (0.1 mmol), additive (0.05 mmol), Pd (10 mol %), base (0.2 mmol), solvent (1 mL), at 120 °C for 24 h. [b]Isolated yields.

With the optimized reaction conditions in hand, we next investigated the substrate scope for the assembly of indole cores employing triarylphosphines to construct the benzoic ring (Scheme 2). The catalytic reaction tolerated a wide range of functionalities, including electron-rich and -deficient aniline derivatives. Anilines with *meta*- and *para*-alkyl and -alkoxy groups participated well in this annulation reaction (**4b**, **4h**, **4i**). Interestingly, *ortho*-, *meta*-, and *para*-halo-substituted anilines were well-tolerated in the current system, affording the desired indoles **4d−g** with suitable handles for further functionalization reactions in yields ranging from 70 to 86%. Fortunately, electron-withdrawing nitro and CF_3 groups were compatible to achieve the reaction, albeit in lower yields (**4j** and **4k**). Fascinatingly, the strategy could be well extended to alkyl amines to afford *N*-alkyl indoles (**4m−r**), which are prevalent in pharmaceuticals and agrochemicals, in moderate to good yields. Next we turned our attention to the scope of arylphosphines. Alkyl-, alkoxy-, and chloro-substituted arylphosphines participated well in this phosphine metathesis reaction, rendering the corresponding indoles **4s−w** in yields exceeding 64%. The structure of representative product **4s** was further confirmed by X-ray analysis (CCDC 2022004). Triarylphosphines bearing electron-withdrawing fluoro- and trifluoromethyl groups also offered the desired indole cores **4x** and **4y** in 72 and 41% yields, respectively. Fortunately, methyl groups at the *meta*-positions were well tolerated under the optimized reaction condition, and the expected indole product **4z** was obtained in moderate yield. Unfortunately, the reaction was unsuccessful with *ortho*-methyl-substituted triarylphosphine. When tris(2-methoxyphenyl)phosphine was used, however, a mixture of 4- and 6-methoxy-substituted indoles was obtained in a combined 70% yield (entry 27, **4aa** and **4aa′**). The results showed that *para*-iodoanisole participated more efficiently than the *ortho*-substituted arylphosphine in the annulation reaction (o/p = 1/5).

Finally, some substituted alkynes were examined, and the desired 2,3-diaryl indoles **4ab** and **4ac** were collected in high yields (entries 28 and 29). Remarkably, with the unsymmetrical 1-phenyl-1-propyne alkyne, the desired products **4ad** and **4ae** were smoothly delivered as single regioisomeric products in 78 and 48% yields, respectively. The high regioselectivity of the reaction may be attributed to the carbopalladation sequence of the alkyne. In this order, the relatively large aryl group of the arylpalladium species approaches the internal alkyne from the less hindered end to

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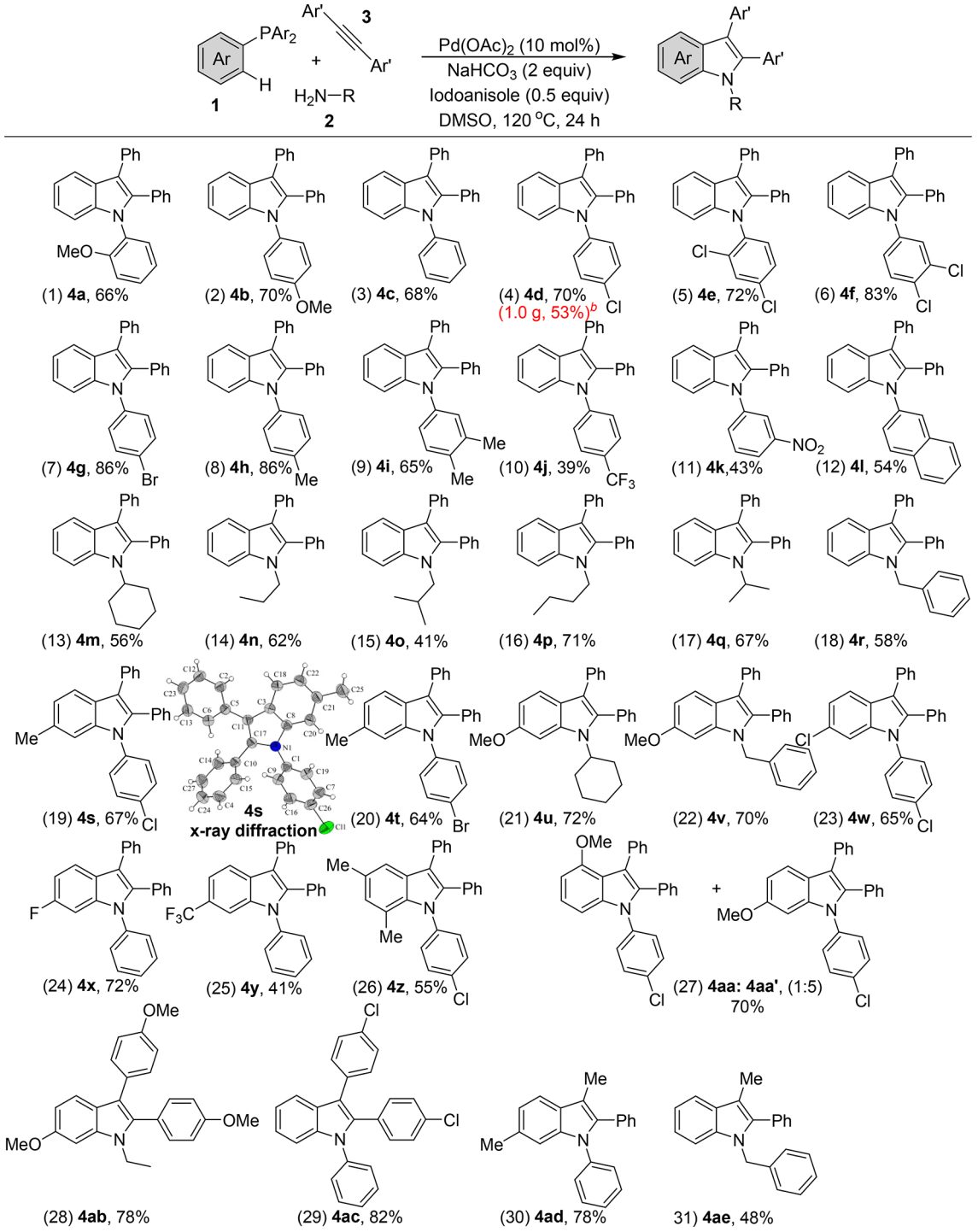
Scheme 2. Substrate Scope for the Construction of Indoles[a]



[a]Reaction conditions: Phosphine (0.1 mmol), aniline **2a** (0.2 mmol), alkyne **3a** (0.1 mmol), iodoanisole (0.05 mmol), $Pd(OAc)_2$ (10 mol %), $NaHCO_3$ (0.2 mmol), DMSO (1 mL), at 120 °C for 24 h. [b]Phosphine (5.0 mmol) was used.

reduce the steric repulsion and replaces the larger group at the C-2 position of the indole ring.[14] Fortunately, when the reaction was scaled up to the gram scale, **4d** was collected in 53% isolated yield.

In the proposed mechanism (Scheme 3), an initial oxidative addition of iodoarene to palladium(0) results in the aryl palladium species **I**. The reductive elimination of phosphine ligand and anisole from the palladium complex to form the phosphonium intermediate followed by the oxidative addition of another carbon−phosphor bond results in aryl group scrambling between aryl groups of phosphine and palladium to form a new palladium-aryl species **II**.[15] Succeeding the exchange process, the carbopalladation reaction of aryl palladium **II** and alkyne[16] followed by an intramolecular C−H functionalization,[17] forms a five-membered palladacycle (**IV**). For the insertion of an amine group into the C,C-palladacycle next, two paths are proposed. A transmetalation between two Pd(II) species, introduced by Cardenas and

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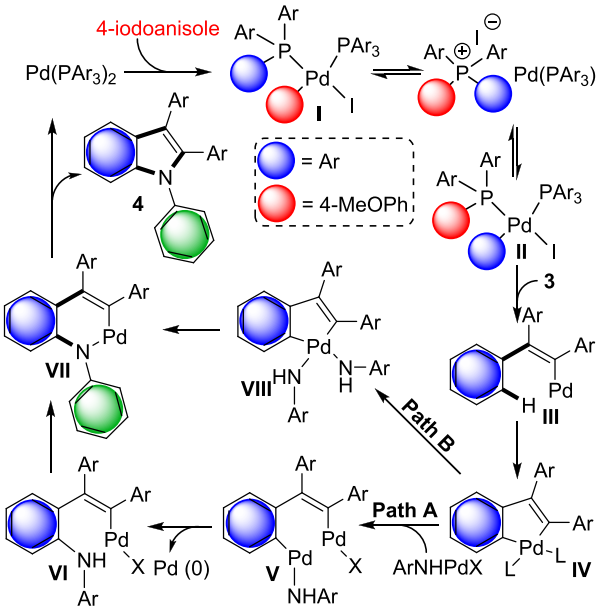
Scheme 3. Proposed Reaction Mechanism



Echavarren[18] and developed by Derat and Catellani[19] (path A), may generate a binuclear palladium species **V**, which upon the reductive elimination of Pd(0) and the successive intramolecular N−Pd bond formation results in Pd(II) species **VII**. A direct trapping of palladacycle with alkyl or arylamines is the next proposed path, which may result in the same palladium−amine complex **VII** (path B). A final reductive elimination reaction releases Pd(0) and makes the indole core **4**.

Overall, although C−P bond scission has a profound impact on the catalyst deactivation and side reactions, we have uncovered its untapped potential in a cascade palladium-catalyzed *ortho*- and *ipso*-functionalization of arylphosphines for the construction of privileged indole scaffolds. The metathesis of Ar−X σ-bonds via a reversible Ar−X oxidative addition/reductive elimination on palladium by means of very simple triaryl phosphines offers a platform to synthesize structurally diverse indoles via the carbopalladation/C−H activation/amination cascade. The approach is scalable and obviates any requisite for large bite angle phosphine ligands to fulfill the C−P bond scission and offers flexible substituents at each point of the indole ring.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03611.

Experimental procedures, optimization, compound characterization data, X-ray data, and $^{1}H/^{13}C$ NMR spectra (PDF)

Accession Codes

CCDC 2022004 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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