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Synthesis of Diaryl Selenides via Palladium-Catalyzed Debenzylative Cross-Coupling of Aryl Benzyl Selenides with Aryl Bromides

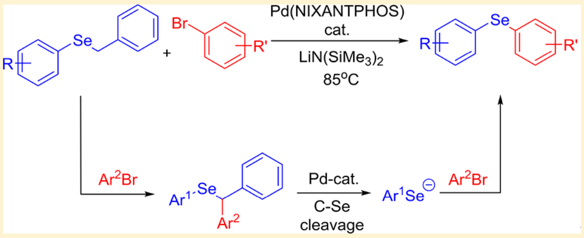
Hao Wang,[†,§] Shuguang Chen,[†,§] Guoqing Liu,[†] Haixing Guan,[†] Daoyin Zhong,[†] Jun Cai,[†]
Zhipeng Zheng,[‡] Jianyou Mao,*[,†] and Patrick J. Walsh*[,†,‡]

[†]Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, 30 South Puzhu Road, Nanjing 211816, P. R. China

[‡]Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, United States

Supporting Information

ABSTRACT: Herein, we report a novel method for synthesizing diaryl selenides from aryl benzyl selenides and aryl bromides via debenzylative cross-coupling with a Pd/NIXANTPHOS-catalyst. NIXANTPHOS outperformed other commonly used bi- and monodentate ligands examined in this novel transformation. This reaction system displays wide functional group tolerance and excellent substrate scope. The transformation broadens the scope of palladium-catalyzed debenzylative processes to use selenolate anions as a leaving group. Its potential for practical synthetic applications was demonstrated with the gram scale synthesis of 4-chlorophenyl phenyl selenide.

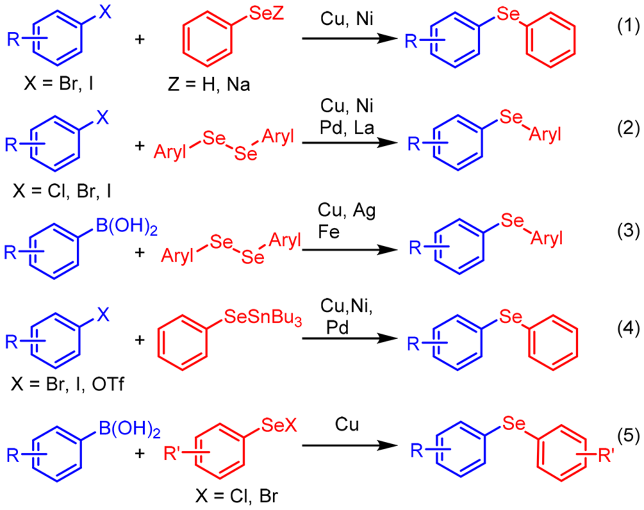


INTRODUCTION

Diaryl selenides constitute an important molecular scaffold with wide applications in natural products, agrochemicals, materials chemistry, and pharmaceutical sciences.[1] Recently, diaryl selenides have also been employed as ligands in transition metal complexes with efficient catalytic activity.[2] Due to the practical applications of diaryl selenides and other selenium-containing compounds, their synthesis has attracted great attention and interest.[3]

Transition metal-catalyzed cross-coupling reactions are the most efficient methods for constructing C−Se bonds in diaryl selenides.[4] These reactions fall mainly into five categories based on the selenium source employed and the reaction mechanism (Scheme 1): (1) transition metal-catalyzed C−Se cross-coupling of phenyl selenol or selenoate with aryl halides;[5] (2) transition metal-catalyzed cross-coupling of aryl halides with diaryl diselenides;[6] (3) transition metal-catalyzed cross-coupling of arylboronic acids with diaryl diselenides;[7] (4) transition metal-catalyzed cross-coupling of phenyl tributylstannyl selenides with aryl halides;[8] (5) or copper-catalyzed cross-coupling of arylselenyl halides with arylboronic acids.[9] These reactions have a number of shortcomings. For example, areneselenols are unstable starting materials that often have unpleasant odors, exhibit a narrow substrate scope, which has been attributed to difficulties in purification of diselenides, or use toxic selenium reagents. Stannyl selenides are also toxic and, therefore, not suitable for large-scale reactions. In order to circumvent some of these drawbacks, it is necessary to explore less traditional approaches that employ more benign organoselenium reagents that can be activated by transition metal-catalysts, ultimately leading to C−Se bond formation.[10]

Scheme 1. Transition Metal-Catalyzed Diaryl selenide Synthesis



Recently, our group initiated studies to arylate sulfenate and thiolate anions via a palladium-catalyzed debenzylative cross-coupling strategy (Scheme 2, eq 1).[11] During our studies of these Pd-catalyzed transformations, we found that van Leeuwen's NIXANTPHOS ligand significantly outperformed other electronically and sterically diverse mono- and bidentate phosphines. It is known that aryl thiolate anions and aryl

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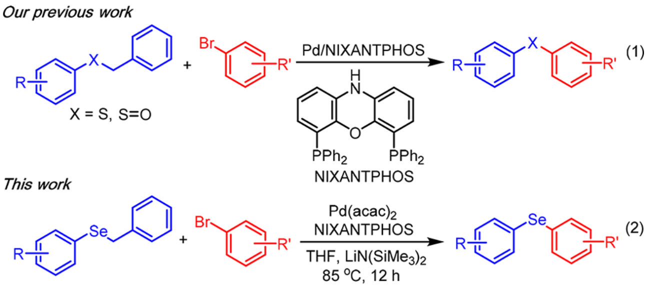
Scheme 2. Palladium-Catalyzed Debenzylative Arylations with Aryl Bromides

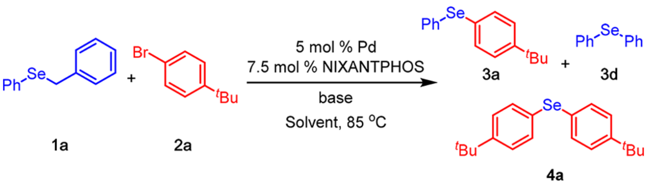


selenolate anions exhibit different reactivity, making it important to study both the chemistry of organosulfur and selenium compounds.[4b,11h,12] Thus, we decided to examine the reactivity of aryl benzyl selenides in the debenzylative cross-coupling reaction. Herein, we disclose the Pd/NIXANTPHOS-catalyzed debenzylative cross-coupling of aryl benzyl selenides with aryl bromides to generate a diverse array of diaryl selenides (Scheme 2, eq 2).

RESULTS AND DISCUSSION

Preliminary Reaction Optimization. To begin optimization of the debenzylative cross-coupling process with phenyl benzyl selenide **1a** and 4-*tert*-butyl bromobenzene **2a**, we examined six different bases [$LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, KO*t*Bu, NaO*t*Bu, and LiO*t*Bu] using $Pd(dba)_2$/NIXANTPHOS to generate the catalyst in tetrahydrofuran (THF) at 85 °C for 12 h (Table 1, entries 1−6). This screen identified $LiN(SiMe_3)_2$ as the lead hit, affording the desired diaryl selenide **3a** in 80% yield, along with the symmetric byproducts **3d** (6%) and **4a** (8%). These products likely arise from Se−C bond metathesis, as described by Morandi and coworkers.[3d] It is noteworthy that in the same reaction of the sulfur analogues no symmetrical diaryl sulfides were detected. These findings highlight the differences in reactivity between sulfur and selenium substrates in these reactions.[11f] Other bases either afforded low yields of **3a** (Table 1, entries 2−4) or did not promote the debenzylative cross-coupling process at all (Table 1, entries 5 and 6). We propose that symmetrical diaryl selenide formation is initiated by oxidative addition of the target product **3a** to the palladium catalyst[3d,13,6i] followed by selenolate exchange.

Table 1. Optimization of the Reaction Conditions[a]



entry	Pd source	base	solvent	yield (%)[a]		
				3a	3d	4a
1	$Pd(dba)_2$	$LiN(SiMe_3)_2$	THF	80	6	8
2	$Pd(dba)_2$	$NaN(SiMe_3)_2$	THF	69	8	18
3	$Pd(dba)_2$	$KN(SiMe_3)_2$	THF	70	8	20
4	$Pd(dba)_2$	KO*t*Bu	THF	51	2	8
5	$Pd(dba)_2$	NaO*t*Bu	THF	0	0	0
6	$Pd(dba)_2$	LiO*t*Bu	THF	0	0	0
7	$Pd(dba)_2$	$LiN(SiMe_3)_2$	CPME	12	1	1
8	$Pd(dba)_2$	$LiN(SiMe_3)_2$	dioxane	20	1	1
9	$Pd(dba)_2$	$LiN(SiMe_3)_2$	DME	68	7	10
10	$Pd(OAc)_2$	$LiN(SiMe_3)_2$	THF	69	6	8
11	$Pd_2(dba)_3$	$LiN(SiMe_3)_2$	THF	83	6	8
12	$Pd(acac)_2$	$LiN(SiMe_3)_2$	THF	86	2	5
13	$[PdCl(ally)]_2$	$LiN(SiMe_3)_2$	THF	80	8	11
14[b]	$Pd(acac)_2$	$LiN(SiMe_3)_2$	THF	58	1	3

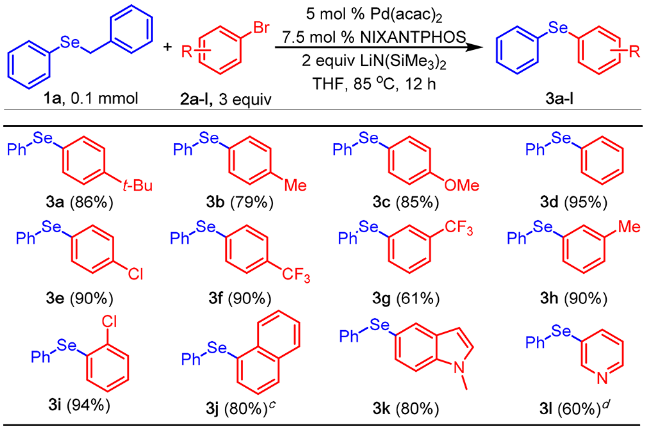
[a]Yields determined by GC analysis of crude mixtures with *n*-dodecane as internal standard. [b]2.5 mol % catalyst was used.

We next screened three different ethereal solvents [CPME (cyclopentyl methyl ether), 1,4-dioxane and DME (dimethoxyethane)] under the conditions of entry 1. Unfortunately, these solvents furnished low yields of **3a** (Table 1, entries 7−9). Based on the solvent screening, THF was identified as the best solvent and was used going forward.

A series of mono- and bidentate phosphines were then tested in the debenzylative cross-coupling process under the conditions of entry 1, and NIXANTPHOS was identified as the most effective (see Supporting Information (SI) for full results). Since palladium sources also can impact reactivity in debenzylative cross-coupling transformations,[11d,f,g] we tested several palladium precursors besides $Pd(dba)_2$, including $Pd(OAc)_2$, $Pd_2(dba)_3$, $Pd(acac)_2$, and $[PdCl(ally)]_2$ (Table 1, entries 10−13). $Pd(acac)_2$ exhibited the highest reactivity, affording the desired product in 86% yield with slightly decreased production of the symmetrical diaryl selenide byproducts (Table 1, entry 12). When the palladium loading was reduced to 2.5%, the yield of **3a** dropped to 58% (Table 1, entries 12 vs 14). Therefore, the best result was obtained with 1 equiv of benzyl phenyl selenide (**1a**), 3 equiv of aryl bromide **2a**, 2 equiv of $LiN(SiMe_3)_2$, 5 mol % $Pd(acac)_2$, and 7.5 mol % NIXANTPHOS in THF at 85 °C for 12 h. It is noteworthy that the catalytic system developed herein is different from our previous reactions with the sulfur analogs [$Pd(acac)_2$ vs $Pd(dba)_2$, $NaN(SiMe_3)_2$ vs $LiN(SiMe_3)_2$, THF vs CPME].[11f]

Scope of Aryl Bromides. With the optimized conditions in hand, we next tested the scope of aryl bromides with phenyl benzyl selenide **1a** (Table 2). In general, the transformation tolerated a broad range of substitution patterns. Aryl bromides bearing electron-donating groups, such as 4-*tert*-butyl

Table 2. Substrate Scope of Aryl Bromides[a,b]

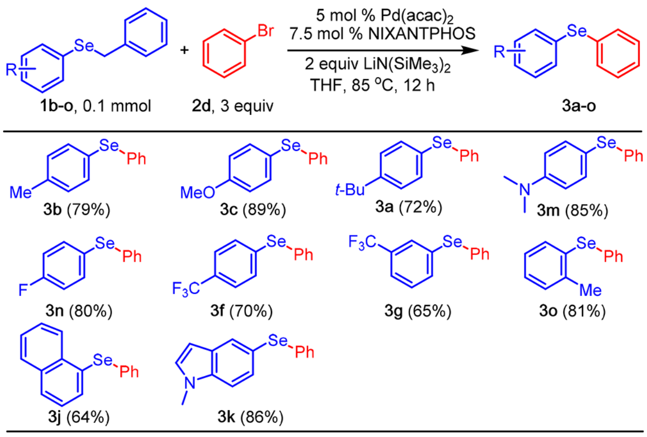


[a]Reactions performed on a 0.1 mmol scale. [b]Isolated yield after chromatographic purification. [c]3 equiv of aryl bromide and 4 equiv of base. [d]10 mol % catalyst.

bromobenzene **2a**, 4-bromotoluene **2b**, and 4-bromoanisole **2c** exhibited very good reactivity, giving the desired products **3a**–**3c** in 79–86% yields. The parent phenyl bromide was an excellent substrate, affording **3d** in 95% yield. Aryl bromides containing electron withdrawing groups, such as 4-chloro (**2e**), and 4-trifluoromethyl (**2f**), also exhibited excellent reactivity, affording both **3e** and **3f** in 90% yield. Aryl bromides with *meta*-substituents, such as 1-bromo-3-trifluoromethylbenzene **2g** and 3-bromotoluene **2h** produced the corresponding products in 61 and 90% yield, respectively, whereas *ortho*-substituted 1-bromo-2-chlorobenzene gave **3i** in 94% yield. It is noteworthy that the chloro substituent in this coupling partner did not participate in the debenzylative transformation. More sterically hindered 1-naphthyl bromide **2j** coupled with **1a** to afford the product **3j** in 80% yield. Diaryl selenides containing indole and pyridine also could be prepared under our conditions, as exemplified by generation of **3k** and **3l** in 80 and 60% yields, respectively.

Scope of Aryl Benzyl Selenides. Next, we turned our attention to the scope of aryl benzyl selenides (Table 3). Aryl benzyl selenides bearing electron-donating groups such as 4-methyl (**1b**), 4-methoxy (**1c**), 4-*tert*-butyl (**1d**), and 4-*N*,*N*-dimethylamino (**1e**) consistently exhibited very good reactivity, giving the target products **3b**, **3c**, **3a**, and **3m** in 72–89% yields. Aryl benzyl selenides containing electron-withdrawing groups were also good coupling partners. 4-Fluorophenyl benzyl selenide **1f** and 4-trifluoromethylphenyl benzyl selenide **1g** afforded the corresponding products in 80 and 70% isolated yields, respectively. *Meta*-substituted 3-trifluoromethylphenyl benzyl selenide **1h** gave the desired product in 65% yield. More sterically hindered 2-tolyl (**1i**) and 1-naphthyl (**1j**) benzyl selenides furnished the products in 81 and 64% yield, respectively, and heterocyclic selenide **3k** could be obtained in 86% yield.

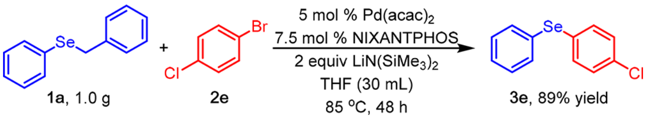
Table 3. Substrate Scope of Aryl Benzyl Selenides[a,b]



[a] Reactions performed on a 0.1 mmol scale. [b] Isolated yield after chromatographic purification.

Gram Scale Reaction. To demonstrate the potential utility of this transformation, a gram scale synthesis of 4-chlorophenyl phenyl selenide **3e** was performed using phenyl benzyl selenide **1a** and 1-bromo-4-chlorobenzene **2e** as coupling partners. The product, which was obtained in 89% yield under our reaction conditions (Scheme 3), provides a readily available handle for further functionalization and elaboration via additional coupling reactions.

Scheme 3. Gram Scale Synthesis of 4-Chlorophenyl Phenyl Selenide



Proposed Mechanism. We next explored the reaction pathway. In this debenzylative transformation, the Pd/NIXANTPHOS catalyst mediates multiple reactions including C(sp^3)–Se bond cleavage and C(sp^2)–Se bond-formation. Based on the experiments outlined below, and our past work with the sulfur analogues, three interdependent Pd-catalyzed reactions are proposed (Figure 1).[11f] Cycle A is the palladium-catalyzed deprotonative cross-coupling process (DCCP) of aryl benzyl selenides with aryl bromides. We have previously demonstrated that aryl benzyl selenides can be reversibly deprotonated by silyl amide bases to generate the carbanion **II**.[12a] Compound **II** undergoes transmetalation with (NIXANTPHOS)Pd(Ar^3)(Br) (**III**) to generate **IV**, which is proposed to undergo reductive elimination to form **V**.

When the coupling in Scheme 4, eq 1 was conducted under the standard conditions, but quenched after 15 min, trace intermediate **5e** was observed by ^{1}H NMR. The structure of compound **5e** was verified by independent synthesis (see SI). We envisioned that the intermediate **5e** quickly undergoes palladium-catalyzed C–Se bond cleavage via an η^3-π-benzyl-palladium intermediate (**VII**, cycle B). To explore the viability of **5e** in the catalytic cycle, independently synthesized **5e** was heated under the standard coupling conditions. After only 15 min, diaryl selenide **3e** was obtained in 79% yield, along with traces of the symmetric products **3d** and **4e** (Scheme 4, eq 2). These results indicate that **5e** is a viable intermediate in this transformation. Unfortunately, we did not detect the proposed diarylmethyl amine product, Ar^{2}Ar^{3}CHNH$_2$, which we expected to be formed on reaction workup. We were also not able to trap this product by addition of benzoyl chloride after hydrolysis to generate the amide. Use of LDA was envisioned to provide a more stable product, Ar^{2}Ar^{3}CHN(*i*-Pr)$_2$. Unfortunately, the debenzylative cross-coupling reaction was not promoted upon substituting LiN(SiMe$_3$)$_2$ by LDA.

In cycle C (Figure 1), the selenolate anion generated from cycle B underwent palladium-catalyzed arylation to form the observed diaryl selenide. We have previously characterized PhSeK•18-crown-6.[12a] In cycle C, we propose PhSeLi undergoes transmetalation with (NIXANTPHOS)Pd(Ar^3)(Br) (**III**) to form the prereductive elimination complex **XI**. Reductive elimination forms the Se–C bond of the product and regenerates Pd(0). This mechanism is consistent with our prior palladium catalyzed debenzylative cross-coupling with aryl benzyl sulfides.[11f]

■ CONCLUSIONS

In summary, a method for the synthesis of diaryl selenides by coupling aryl benzyl selenides with aryl bromides via a palladium-catalyzed debenzylative process has been developed. One advantage of this approach is the in situ generation of the highly reactive aryl selenolate using simple benzyl as a mask to avoid employing areneselenol and aryl tributylstannyl selenide. A wide range of electron-donating and withdrawing aryl substrates, including heterocycles, are well tolerated in our reaction system. The practical synthetic value of this method

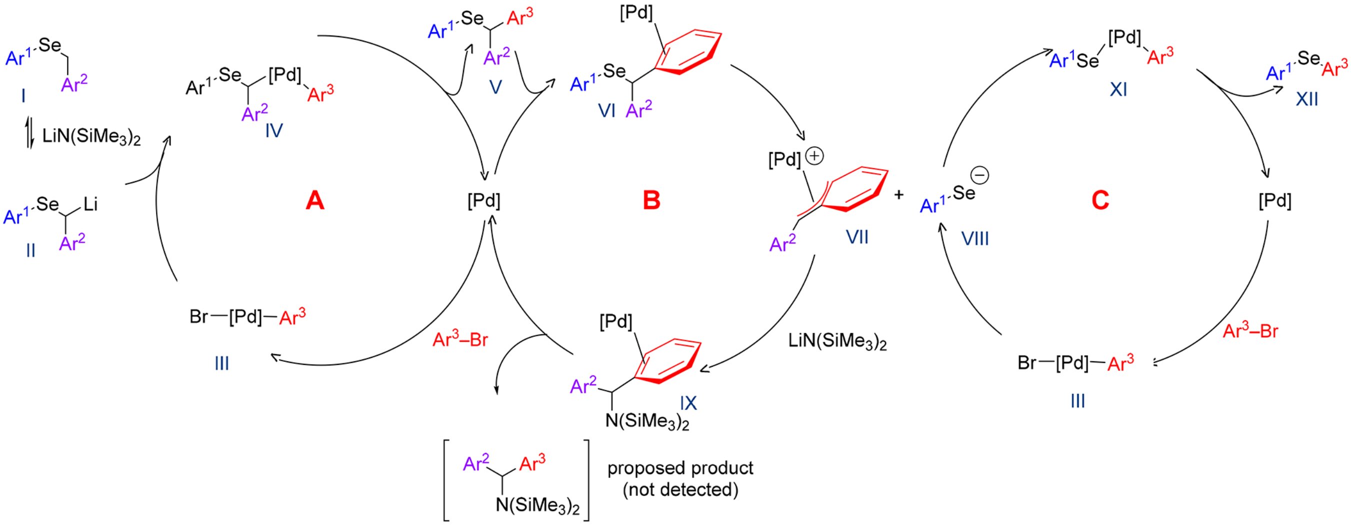
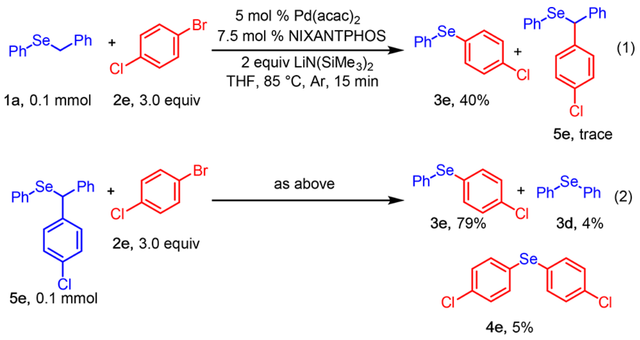


Figure 1. Proposed catalytic cycles for the production of diaryl selenides. Formation of diarylmethyl aryl selenide (cycle A), formation of η^3-π-benzyl-palladium intermediate (cycle B), formation of diarylselenide (cycle C).

Scheme 4. Tandem Synthesis of 4-Chloropheny Phenyl Selenide



has been demonstrated with a gram scale reaction. This transformation also enlarges the scope of transition-metal-catalyzed debenzylative process using selenolate anion as a leaving group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00644.

Experimental procedures, characterization data, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*(J.M.) E-mail: ias_jymao@njtech.edu.cn.

*(P.J.W.) E-mail: pwalsh@sas.upenn.edu.

ORCID

Jianyou Mao: 0000-0003-0581-3978

Patrick J. Walsh: 0000-0001-8392-4150

Author Contributions

[§]H.W. and S.C. contributed equally.

Notes

The authors declare no competing financial interest.

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