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Copper(I)-catalyzed arylselenylation of aryl bromides and iodides

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Abstract—A new protocol to prepare unsymmetrical diarylselenides using the reaction of aryl bromides and iodides with easily available $Bu_3SnSeAr$ catalyzed by Cu(I) complexes under rather mild conditions and with a very high yield is described.

Several synthetic procedures are available for the formation of aromatic carbon–selenium bonds.[1] However, there is a high demand for a general and convenient method for the synthesis of aryl selenides, especially using more available aryl halides (aryl bromides instead of iodides) and inexpensive catalysts. Aryl bromides may be used as a source for the synthesis of diaryl selenides via their conversion to the corresponding aryllithium or magnesium compounds and subsequent reaction with diaryldiselenides.[2] However, this synthetic approach has many significant limitations, such as the availability of the corresponding organometallic compounds.

Previously we and others have shown that easily available tributyltin aryl selenides $Bu_3SnSeAr$ **1**[3] are an excellent source of an arylselenyl group in nucleophilic substitution (S_N2) reactions[4] and in the arylselenylation of aryl halides and triflates catalyzed by palladium[5] and nickel[5a,b] complexes, respectively. However, unlike the group of Nishiyama[5c] we had not succeeded in carrying out cross-coupling of $Bu_3SnSePh$ **1a** with PhCl or even with ArBr. According to our data[5b] the formation of Ph_2Se **2a** reported by the authors[5c] is related to the Pd-catalyzed disproportionation of **1a** (Scheme 1).

$$\underset{\textbf{1a,b}}{2\,Bu_3SnSeAr} \xrightarrow{[cat]} \underset{\textbf{2a,b}}{Ar_2Se} + (Bu_3Sn)_2Se$$

$Ar = Ph(a),\ 4\text{-}FC_6H_4(b)$

Scheme 1.

In the present report we show that the cross-coupling of aryl iodides and bromides with the tributyltin arylselenide **1b** gives high product yields with catalysis by nickel, and especially copper complexes (Table 1). The reaction of 4-iodoacetophenone **3a** with 4-$FC_6H_4SeSnBu_3$ **1b** (DMF or toluene, 95–110°C) was chosen for the screening of the catalytic systems (Table 1, entries 1–8). Compared to the palladium phosphine complex, which efficiently and selectively catalyzes this reaction (entry 1), the corresponding nickel complexes are ineffective and lead to the formation of the disproportionation product $(4\text{-}FC_6H_4)_2Se$ **2b** together with the cross-coupling product **4a** (entries 2, 3). The results with the $(phen)_2NiBr_2$ (phen = 1,10-phenanthroline) complex were also rather disappointing (entry 4), but the use of the complex $(bpy)_2NiBr_2$ (bpy is 2,2′-bipyridine), resulted in the complete conversion in 8 h with high selectivity (91% yield of **4a**, entry 5). Excellent results were achieved with the copper complexes CuI·phen and (Ph_3P)CuI·phen (entries 7, 8), which allowed us to carry out the reactions with near quantitative yields of diaryl selenide **4a** and with 100% selectivity.

We have also carried out the arylselenylation reaction with an activated aryl bromide 4-$CF_3C_6H_4Br$, which was not possible using Pd catalysis (entry 9), using the catalytic system which had showed maximum efficiency in the benchmark reaction with the aryl iodide. Yet the nickel complex $(bpy)_2NiBr_2$ turned out to be inefficient and besides the product of cross-coupling **4b** (52%)

Keywords: diaryl selenides; arylselenation; aryl halogenides; copper-catalyzed; nickel-catalyzed; trialkyltin aryl selenides.

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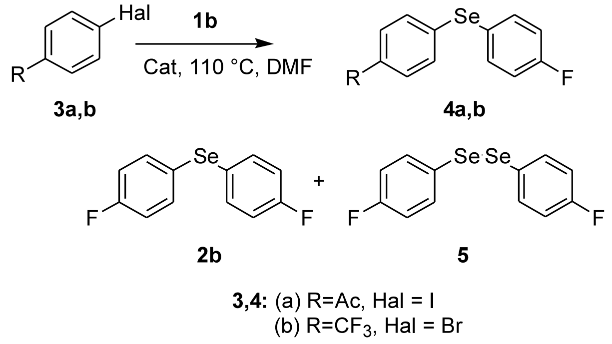


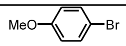
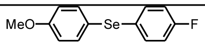
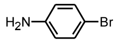
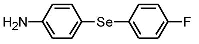
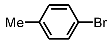
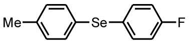
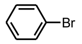
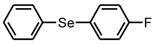
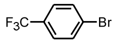
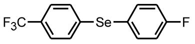
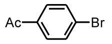
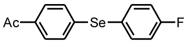
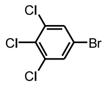
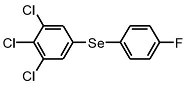
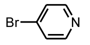
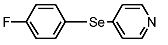
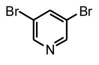
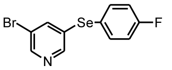
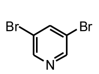
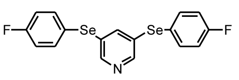
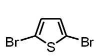
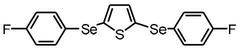
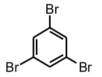
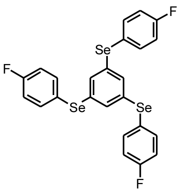
Scheme 2.

gave the disproportionation **2b** and oxidation products **5** (entry 10). According to Christau and co-workers[6] the similar reaction with alkali arylselenolates is a highly selective one.

The efficiency of the copper complex $(Ph_3P)CuI{\cdot}phen$ was again impressive: complete conversion was achieved after 8 h with 97% yield (entry 11). This was in contrast to the earlier report,[7] when the complex of CuI with neocuproine (2,9-dimethyl-1,10-phenanthroline) failed to catalyze the reactions of aryl selenoles with aryl bromides. A recently described[8] arylselenylation by $(ArSe)_2$ in the presence of Mg catalyzed by Cu(I) is also limited to aryl iodides.

Having found the optimum reaction conditions we carried out the reactions of tributyltin arylselenide **1b** with various aryl and hetaryl bromides, having both electron withdrawing and electron donating substituents (Scheme 3, Table 2).[9] Yields of unsymmetrical diaryl selenides were exceedingly high (86–94%) in all the cases, and even 4-bromoaniline (entry 2) was no exception. However, the arylselenylation of aryl bromides with electron donating substituents required a longer reaction time.

Table 2. Reaction of aryl bromides and $4\text{-}FC_6H_4SeSnBu_3$

Entry	ArBr	$4\text{-}FC_6H_4SeAr$	T, h	Yield[a] (%)
1			16	90 (87)
2			16	86 (75)
3			12	90
4			12	94
5			6	92 (86)
6			6	89
7			6	94 (90)
8			4	82 (75)
9			4	72 (65)[b]
10			6.5	95 (88)
11			5	90 (83)
12			27	73 (67)

[a] Yield according to ^{19}F NMR data. Isolated yield given in parentheses;

[b] 0.9 eq of **1b** was used

Table 1. Optimization of the reaction between aryl halides and tributyltin arylselenide **1b** (Scheme 2)[a]

Entry	Catalyst	ArX	T (h)	Conv. (%)	Yield[b] (%)		
					4	**2b**	**5**
1	$(Ph_3P)_2PdCl_2$[c,d]	**3a**	5	100	96	0	0
2	$(Ph_3P)_2NiCl_2$	**3a**	8	42	14	28	0
3	$(Ph_3P)_2NiBr_2$	**3a**	8	45	19	26	0
4	$(phen)_2NiBr_2$	**3a**	10	47	37	10	0
5	$(bpy)_2NiBr_2$	**3a**	8	100	91	7	0
6	CuI+phen[e]	**3a**	15	65	59	6	0
7	CuI+phen	**3a**	6	100	100	0	0
8	$(Ph_3P)CuI$+phen	**3a**	6	100	100	0	0
9	$(Ph_3P)_4Pd$[d,e,f]	**3b**	15	70	0	45	0
10	$(bpy)_2NiBr_2$	**3b**	12	100	52	18	10
11	$(Ph_3P)CuI$+phen	**3b**	8	100	97	0	3

[a] Reaction conditions: 1 mmol of ArHal, 1 mmol of **1b**, 10 mol% of catalyst, 2 ml of dry DMF heated at 110°C under argon.

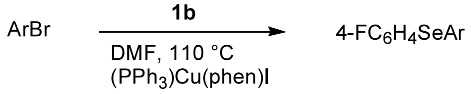
[b] Yield and product ratio according to ^{19}F NMR.

[c] 1.5 mol% of catalyst.

[d] 95°C.

[e] Solvent: toluene.

[f] 5 mol% of catalyst.



$$\mathrm{ArBr}\xrightarrow[\text{DMF, 110 °C}\ (\mathrm{PPh_3})\mathrm{Cu(phen)I}]{\mathbf{1b}}4\text{-}\mathrm{FC_6H_4SeAr}$$

Scheme 3.

For the substrates having two or three bromine atoms, one can selectively substitute one bromine (using an excess of ArBr, entry 9), or substitute all the bromine atoms using the appropriate reagent ratio (entries 10–12), though the substitution of all three bromine atoms in 1,3,5-tribromobenzene require prolonged heating (entry 12).

In summary, a new protocol for the synthesis of diaryl selenides from aryl bromides and $Bu_3SnSeAr$ is described. The reaction is catalyzed by copper complexes and allows one to obtain the arylselenylation products in high yields from a large variety of aryl bromides.

Acknowledgements

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9. **General procedure**: In a Schlenk tube under argon were placed ArBr (1.0 mmol), $(PPh_3)CuI$ and phenanthroline (10 mol% of each with respect to bromide), 4-$FC_6H_4SeSnBu_3$ (1.05 equiv. with respect to bromide, unless otherwise noted) and 2.0 ml of dry DMF. This mixture was stirred at 110°C for the appropriate time. Then the reaction mixture was treated with aqueous KF to remove organotin compounds, and was extracted with ether. The crude product was purified by flash column chromatography on silica gel (eluent: hexane or hexane/CH_2Cl_2 8:2) to give the analytically pure diarylselenide. All synthesized compounds were characterized by ^{1}H, ^{13}C, ^{19}F, ^{77}Se NMR spectroscopy and by elemental analysis.