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A Highly Efficient and Air-Insensitive Copper-Catalyzed Synthesis of Diorganyl Chalcogenides

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Abstract

CuI-C22 complex, has been reported as a highly-active, efficient catalyst based on copper(I), for the synthesis of diorganyl- monochalcogenides. In addition to thermal- and air-stability, facile preparation of this homogeneous copper(I) catalyst, the corresponding products obtained in good to excellent yields and with the short reaction times. Remarkably, it was observed that diaryl/dialkyl dichalcogenides could be successfully cross-coupled with electronically and sterically diverse arylboronic acids.

Keywords

Diorganyl chalcogenides; cross-coupling; homogeneous catalyst; aryl boronic acids

Introduction

The creation of the Aryl-heteroatom bond is very important in various pharmaceutical, industrial and synthetic fields.¹ Moreover, many organic molecules containing S, Se, and Te in their structures have been employed as reagents,² ionic liquids,³ catalysts,⁴ and ligands for transition metals⁵ so far. Among the C_{aromatic}-X bonds, the formation of C-Se and C-S bonds are attractive synthetic targets, mainly owing to their potential therapeutic applications as anti-cancer, antiviral, antimicrobial, antitumor, and antioxidant.⁶ In recent years, many methods have been developed for the synthesis of these classes of compounds. Traditional methods for the preparation of C_{aromatic}-chalcogen include various steps that often require photochemical reaction conditions or hard reaction conditions, such as the use of polar and toxic solvents such as hexamethyl phosphite trichloride (HMPA), long reaction times, and high temperatures.⁷ In recent years, transition metal-catalyzed methodologies played a pivotal role in C_{aromatic}-Y (Y = S, Se, Te) bond formation reactions. Various metal sources including Ni,⁸ Pd,⁹ Fe,¹⁰ Zn,¹¹ and Cu¹² have been utilized to associated with a ligand as a carbon-chalcogen-bonded catalyst for the synthesis of diaryl chalcogenides. The most common methods mediated by transition metals for the preparation of diorganyl monochalcogenide involve: (a) coupling reaction of aryl halides with alkyl/aryl dichalcogenides,^{8a,11,12b-e} (b) reaction of diorganyl dichalcogenides with organometallic reagents,¹³ and (c) C-H activation of arenes with appropriate chalcogen source.¹⁴ Employing dichalcogenides as substrate in the synthesis of diorgano monochalcogenide facilitate the reaction conditions, since they are stable in air and easy to handle. Organoboronic acids can be considered as preferred coupling partner, since they are generally non-toxic, air-stable, commercially available, compatible with a variety of functional groups, and

easy to handle compounds. Meanwhile, under catalytic amount of metal sources, they can easily undergo the boron-to-metal exchange reaction.¹⁵ Comparing to organoboronic acids, the activation of aryl halides is difficult and requires to use high equivalents of base or an additive as reductant.¹⁶ Consequently, the cross-coupling reaction of diorganyl dichalcogenides with organoboronic acids can be considered as a straightforward synthetic route for the construction of C_{aromatic}-Y bond. In this context, the first cross-coupling reactions of diorganyl dichalcogenides with organoboronic acids were reported by Wang and Taniguchi groups.¹⁷ The above-mentioned reactions were performed in the presence of copper as a cost-effective and low-toxic catalyst without using any additive, and various symmetrical and unsymmetrical diorganyl monochalcogenides were prepared. Subsequently, several researches have been conducted to improve the cross-coupling reaction of diorganyl dichalcogenides with organoboronic acids.

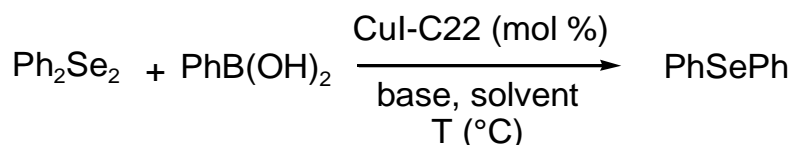
we demonstrated that the complexes of Cu(I) with the commercially available diazacrown ether, 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Kryptofix® 22 or cryptand-22) operate as active homogeneous catalysts under aerobic conditions. We thought that the chelating effect of such N- and O-containing ligand may assist in stabilizing the reactive copper intermediates. The first combination of CuI-C22 was synthesized by Mühle and Sheldrick;¹⁸ however, a substitute and more easily synthetic route was replaced by our research team to provide this complex.¹⁹ We now wish to report a new heat-, and air-stable and efficient homogeneous copper(I) iodide cryptand-22 complex (CuI-C22) for the synthesis of organic building blocks containing S, Se, and Te in their structures.²⁰

Results and Discussion

CuI-C22-catalyzed synthesis of diaryl chalcogenides

In order to optimize the reaction conditions including solvent, base, temperature and the amount of the catalyst, in order to find the best yield for the synthesis of diaryl chalcogenides, the cross-coupling reaction of diphenyl diselenide with phenylboronic acid was selected as a model reaction. As summarized in Table 1, various organic and inorganic bases were tested and the highest yield of the final product was obtained in the presence of KOH (Table 1, entry 2). When K_2CO_3 and NaOH were employed, diphenylselenane was produced in 18 and 88% yields, respectively (Table 1, entries 1 and 3). On the other hand, 93% yield of the desired product was achieved, when K_3PO_4 was utilized as the base, whereas the coupling reaction proceeded slowly and completed after 10 h (Table 1, entry 4).

Table 1: Optimization of the conditions for the reaction of diphenyl diselenide with phenylboronic acid.^a



Entry	Base	Solvent	T (°C)	CuI-C22 Cat. (mol %)	Time (h)	Yield (%) ^b
1	K_2CO_3	DMF	110	3.3	12	18
2	KOH	DMF	110	3.3	2	96
3	NaOH	DMF	110	3.3	8	88
4	K_3PO_4	DMF	110	3.3	10	93
5	DIPEA	DMF	110	3.3	24	N.R.
6	KOH	DMSO	110	3.3	17	88
7	KOH	PEG	110	3.3	10	97
8	KOH	Toluene	110	3.3	24	N.R.
9	KOH	H ₂ O	110	3.3	24	N.R.
10	KOH	DMF	100	3.3	2	90
11	KOH	DMF	90	3.3	15	90

12	KOH	DMF	120	3.3	2	92
13	KOH	DMF	110	1.65	6	83
14	KOH	DMF	110	2.2	6	85
15	KOH	DMF	110	2.7	6	88
16	KOH	DMF	110	2.9	5	90
17	KOH	DMF	110	3.1	2	89
18	KOH	DMF	110	3.2	2	91
19	KOH	DMF	110	3.85	4	94

^aReaction conditions: diphenyl diselenide (0.2 mmol), phenylboronic acid (0.4 mmol), base (0.4 mmol), solvent (1 mL), CuI-C22 Cat. (mol%), and T (°C).

^b Isolated yields

Furthermore, no conversion of the starting materials was observed, when N,N-diisopropylethylamine (DIPEA) was used as the base (Table 1, entry 5). The effect of the solvent was also screened (Table 1, entries 6-9). It was found that among the various solvents examined such as N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), polyethylene glycol-400 (PEG-400), and water, various solvents examined such as N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), polyethylene glycol-400 (PEG-400), and water, DMF is the best reaction medium for this transformation (Table 1, entry 2).

Regarding the effect of temperature on reaction speed, optimization of reaction temperature was also put on the agenda. It can be concluded that the corresponding product was produced in 96% during 2 h at 110 °C (Table 1, entry 2). Higher and lower temperatures resulted in either lower yields or longer reaction times (Table 1, entries 10-12).

The reaction was also performed using different amounts of CuI-C22 catalyst over the range of 1.65-3.85 mol% (Table 1, entries 13-19). It can be seen that the best conversion was obtained when 3.3 mol% of the catalyst was used (Table 1, entry 2). However, lower amount of the catalyst, resulted in extending the reaction time as well as diminishing the yield of the corresponding product.

According to the optimum conditions, we examined the versatility of the CuI-C22 catalyst in the cross-coupling reaction of various diorganyl dichalcogenides with arylboronic acids (Table 2). As shown in Table 2, diverse R₂Y₂ (Y = S, Se, Te) substrates were cross-coupled successfully with arylboronic acids, regardless of the substituents.

Table 2: CuI-C22-catalyzed cross-coupling reaction of diorganyl dichalcogenides with arylboronic acids.^a

Entry	(RY) ₂	Ar	Time (h)	Yield (%) ^b
1	(C ₆ H ₅ Se) ₂	C ₆ H ₅	3	96
2	(C ₆ H ₅ Se) ₂	4-MeC ₆ H ₄	2.5	92
3	(C ₆ H ₅ Se) ₂	2-MeC ₆ H ₄	3	87
4	(C ₆ H ₅ Se) ₂	4-MeOC ₆ H ₄	1	98
5	(C ₆ H ₅ Se) ₂	2-MeOC ₆ H ₄	3.5	84
6	(C ₆ H ₅ Se) ₂	2,4,6-Me ₃ C ₆ H ₂	4	82
7	(C ₆ H ₅ Se) ₂	n-C ₄ H ₉	4	86
8	(C ₆ H ₅ Se) ₂	4-ClC ₆ H ₄	4	89
9	(C ₆ H ₅ Se) ₂	4-FC ₆ H ₄	5	88
10	(4-ClC ₆ H ₄ Se) ₂	C ₆ H ₅	3	94
11	(4-ClC ₆ H ₄ Se) ₂	4-MeOC ₆ H ₄	2	95
12	(4-ClC ₆ H ₄ Se) ₂	4-ClC ₆ H ₄	3	91
13	(2-MeC ₆ H ₄ Se) ₂	4-MeOC ₆ H ₄	5	85
14	(C ₆ H ₅ CH ₂ Se) ₂	4-ClC ₆ H ₄	4	82
15	(C ₆ H ₅ S) ₂	4-MeC ₆ H ₄	4	86
16	(C ₆ H ₅ S) ₂	2-MeC ₆ H ₄	6	81
17	(C ₆ H ₅ S) ₂	4-MeOC ₆ H ₄	4	88

18	(C ₆ H ₅ S) ₂	4-ClC ₆ H ₄	5.5	83
19	(4-MeC ₆ H ₄ S) ₂	C ₆ H ₅	4.5	82
20	(4-MeC ₆ H ₄ S) ₂	4-MeOC ₆ H ₄	5	84
21	(C ₆ H ₅ CH ₂ S) ₂	4-ClC ₆ H ₄	7	78
22	(<i>n</i> -C ₄ H ₉ S) ₂	C ₆ H ₅	9	74
23	(C ₆ H ₅ Te) ₂	4-MeOC ₆ H ₄	2	92

^a Reaction conditions: (RY)₂ (0.2 mmol), arylboronic acid (0.4 mmol), KOH (0.4 mmol), CuI-C22 (3.3mol%), DMF (1 mL) at 110 °C.

^b Isolated yield.

To probe the substrate scope, the coupling reaction of diaryl diselenides with arylboronic acids bearing electron-donating and electron-withdrawing substituents were studied (Table 2, entries 1-14). It was observed that electron-rich arylboronic acids underwent C-Se bond formation reaction smoothly to produce the corresponding products in high to excellent yields (Table 2, entries 2-6, 11, 13). Moreover, the coupling reaction of arylboronic acids with electron-donating groups attached at ortho-position resulted in longer reaction times and lower of coupling partner. Furthermore, more sterically demanded 2,4,6-trimethylphenylboronic acid afforded the desired product in 82% isolated yield (Table 2, entry 6). Chemoselectivity of our approach was examined using diaryl dichalcogenides and arylboronic acids containing halide substituents (Table 2, entries 8, 9, 12, 14). For instance, diphenyl diselenide reacted with 4-chloro- and 4-fluorophenylboronic acid in 89% and 88% yields (Table 2, entries 8 and 9), respectively and no side-product(s) was observed. Meanwhile, bis(4-chlorophenyl) diselenide was cross-coupled with 4-chlorophenylboronic acid to generate bis(4-chlorophenyl)selane in 91% (Table 2, entry 12). Dibenzyl diselenide as aliphatic

substrate reacted efficiently with 4-chlorophenylboronic acid furnishing the desired product in 82% yield (Table 2, entry 14). To extent the scope of the current protocol, C-S coupling reaction of diorganyl disulfide with arylboronic acids was also surveyed (Table 2, entries 15-22). Comparing to diselenide counterparts, the cross-coupling reaction of disulfides occurred slower with lower yields, which is due to the higher bond dissociation energy of S-S bond. However, applying the same reaction conditions wide range of diorganyl disulfides reacted with arylboronic acids. A remarkable observation was the cross-coupling reaction of less reactive dialkyl disulfide with arylboronic acid, obtaining the final products in good yields (Table 2, entry 22). As shown in Table 2, all C-S cross-coupling reactions occurred smoothly and were not affected by the nature or steric hindrance of functional groups on the back bone of the substrates. Also ditelluride as chalcogen sources reacted with arylboronic acids, which converted to the desired products in 92-% during 2h (Table 2, entry 23).

Conclusion

In this paper, the cross-coupling reaction of diaryl/dialkyl dichalcogenides with arylboronic acids has been carried out in the presence of CuI-C22 complex. It has been shown that copper(I) iodide complex with cryptand-22 is the robust, air- and moisture-insensitive catalyst, which can be successfully utilized in the Csp^2-Y (Y = S, Se, Te) bond formation reactions. The corresponding symmetrical and unsymmetrical diorganyl monochalcogenides bearing various functional groups have been produced in 74-98% yields within 1-9 h.

Experimental

General procedure for the synthesis of diorganyl monochalcogenides:

A test tube equipped with magnetic stirrer bar was charged with diorganyl dichalcogenide (0.2 mmol), CuI-C22 catalyst (3.3 mol%), and DMF (1 mL). Then KOH (0.4 mmol) and arylboronic acid (0.4 mmol) was added to the above mixture and stirred for appropriate time at 110 °C (as depicted in Table 2). After completion of the reaction, monitored by thin layer chromatography (TLC), the reaction mixture was cooled down to room temperature and extracted with CHCl₃ (2 × 5 mL). The combined organic layers were rinsed with H₂O (2 × 5 mL), dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (eluent: n-hexane) to afford the final product in pure form.

Supporting Information

Supporting information text

Supporting Information File 1:

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Title: A Highly Efficient and Air-Insensitive Copper-Catalyzed Synthesis of Diorganyl Chalcogenides

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