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Short communication

New arylselanylpyrazole-copper catalysts: Highly efficient catalytic system for C—Se and C—S coupling reactions

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ABSTRACT

We describe herein the use of arylselanylpyrazole–copper complexes as versatile catalysts for C—Se and C—S coupling reactions. The performance of these complexes for C—Se reactions was investigated in chalcogenoacetylene synthesis. The reactions were carried out under mild and aerobic conditions and afforded selanylalkynes bearing a variety of electron-withdrawing and electron-donating groups. The performance of these catalysts for C—S coupling was investigated through the reaction of aryl halides with thiols and products were obtained in moderate to excellent yields. A plausible mechanism for selenoacetylene synthesis is also suggested, and the ^{77}Se NMR results show that these arylselanylpyrazole ligands act as hemilabile ligands. High-resolution mass spectrometry was used to investigate the intermediates and also to corroborate the proposed catalytic cycle.

1. Introduction

Copper-catalysed reactions have re-emerged in recent decades, aiming to resolve two main points: (*i*) substitution for palladium catalysis, mostly because of toxicity, availability and cost, and (*ii*) cross-coupling reactions in which copper works in a way strikingly similar to palladium and/or possesses unique chemoselectivity and reactivity [1,2]. In this context, many carbon–carbon and carbon–heteroatom bond-formation reactions based on copper catalysis have been developed which are cheaper and possess higher reserves and low toxicity.

Since Glaser's findings, in 1869, of terminal alkyne homocoupling using copper chloride [3], a series of important copper-catalysed protocols has been reported. Copper chemistry, which gradually became neglected in the 1970s when it was discovered that catalytic amounts of palladium permited reactions to occur at lower temperatures [4], has re-emerged in recent decades in research using soluble copper salts and ligand-coordinated Cu complexes [5]. This new generation of copper-based catalysts, together with an understanding of mechanisms and the development of novel ligands, has provided a wide variety of different reactions under milder conditions with desirable yields and excellent functional-group tolerance [5].

Ullmann-type reactions for the synthesis of ethers [6], amines [7], sulfides [8], and selenides [9], respectively (Scheme 1), illustrate that copper complexes are powerful tools in organic synthesis. Scheme 1 also shows some ligand structures employed in coupling reactions; the number of molecules used for this purpose is much larger, and includes Schiff bases, oximes, β-ketoesters, 1,3-diketones, L-proline, 1,2-diamine, phenanthroline and derivatives, and phosphorus-containing structures [5].

Alkynylselenides have already been used in several reactions as intermediates, for example, in hydration [10], hydrohalogenation [11], hydrosulphonation [12], electrophilic cyclization [13], electrocyclization [14], and hydroboration [15], among others. General synthetic methodologies for alkynylselenides involve reactions between terminal alkynes and diorganyl diselenides and use strong bases or organometallic reagents. Variation of these protocols is associated with other alkyne species like bromoalkynes [16] and propiolic acid derivatives [17] or electrophilic selenium species [18]. In recent years, novel protocols have been reported using transition metal catalysts as substitutes for organometallic reagents. These studies evaluated copper, as mentioned above, iron [19], indium [20], and silver [21] as catalytic systems for this purpose. However, in general, the main drawbacks presented are related to functional-group tolerance, long reaction times, and the use of specific alkynes or selenium species, etc.

This work focuses on carbon–heteroatom bond formation, in particular carbon–selenium and carbon–sulfur. A number of synthetic methodologies for organochalcogenides in general has accompanied the growth of copper catalysis. While organoselenium compounds have been investigated for use as intermediates in organic reactions, organosulfides have consolidated their applications in pharmaceuticals

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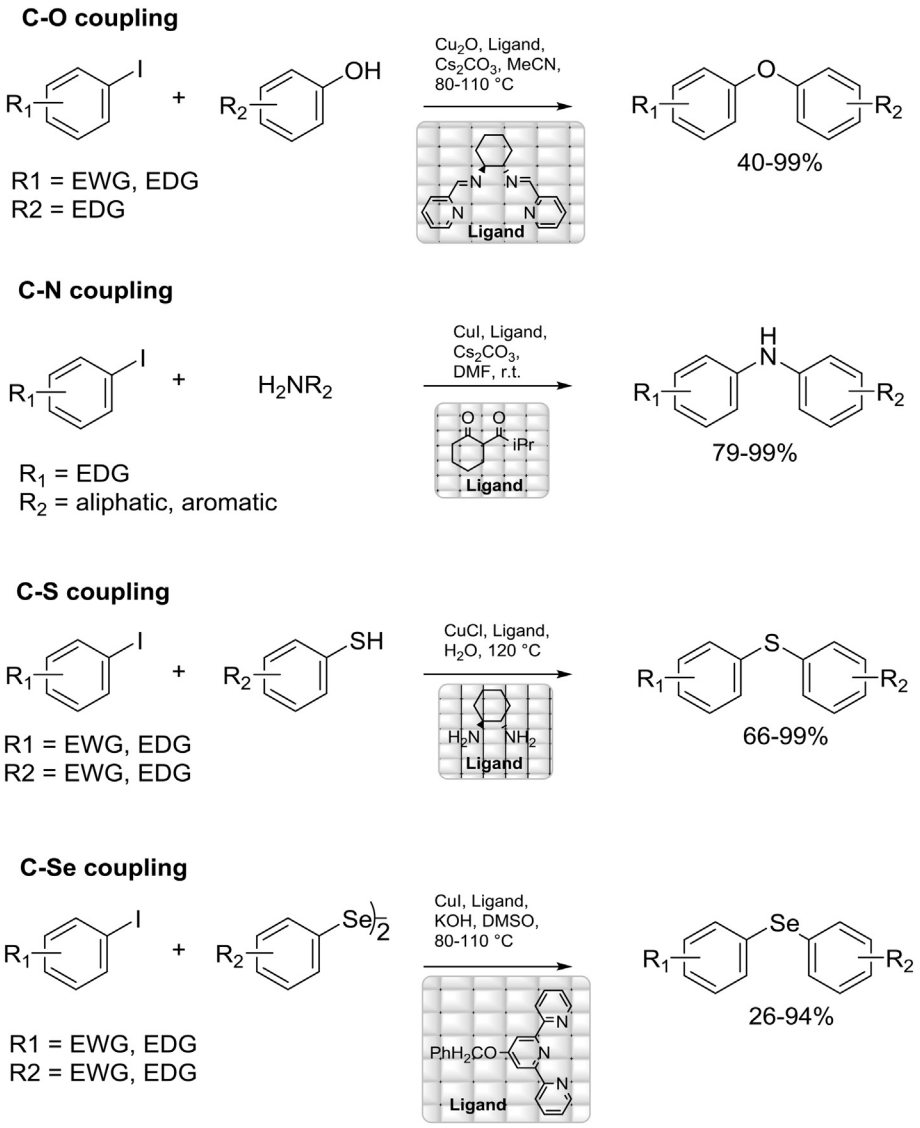


Scheme 1. Carbon–heteroatom coupling reactions catalysed by copper complexes.

[22]. In this context, promising results for selanylpyrazoles as ligands to nickel in oligomerization [23] prompted us to examine selanylpyrazole–copper complexes in carbon–selenium and carbon–sulfur coupling for synthesis of alkynylselenides and aryl sulfides, respectively.

This fact, combined with our continuous interest in the synthesis of organoselenium compounds [24], prompted us to explore mild and efficient coupling reactions for carbon–selenium and carbon–sulfur bond formation catalysed by copper–selanylpyrazole complexes.

2. Experimental

2.1. General information

All reactions and manipulations for sulfide and selenoacetylene preparation were performed under aerobic conditions. The NMR spectra were recorded on a 400 MHz spectrometer Varian Inova 400 and a Bruker Avance 400. Chemical shifts (δ) are expressed in ppm with TMS as internal standard for $CDCl_3$. Coupling constants are reported in Hz. The ^{77}Se NMR spectra were recorded with diphenyl diselenide as internal standard (reference signal at 463 ppm). HRMS spectra were obtained in a Micromass Q-Tof micro mass spectrometer. All the column chromatography separations were done using silica gel 230–400 Mesh. Solvents were purified by the usual methods. Other reagents were obtained from commercial sources and used without further purification.

2.2. General procedure for selanylpyrazoles synthesis

Step 1: A mixture of 3,5-dimethylpyrazole (1.92 g, 20 mmol) and paraformaldehyde (0.60 g, 20 mmol) was heated for 48 h. The crude reaction was purified by sublimation affording 1-(2-hydroxymethyl)-3,5-dimethylpyrazole as a white solid in 85% yield. Step 2: The reaction was performed under argon by using standard Schlenk techniques. To a cold (0 °C) solution of 1-(2-hydroxymethyl)-3,5-dimethylpyrazole (1.0 g, 8 mmol) in chloroform was added dropwise thionyl chloride (1.15 mL in 15 mL of $CHCl_3$) and the mixture was refluxed for 4 h. The precipitate (1-(2-chloromethyl)-3,5-dimethylpyrazole, 79% yield) was collected, washed with diethyl ether and dried. Step 3: The reaction was also performed under argon by using standard Schlenk techniques. To a solution of the respective diaryl dichalcogenide (1.5 mmol) in ethanol/THF (5:15 *v*/v) was added $NaBH_4$ (0.126 g, 3.3 mmol). After 30 min, 1-(2-chloromethyl)-3,5-dimethylpyrazole (0.317 g, 2.0 mmol) was added and reaction mixture was stirred for 24 h at 70 °C. The crude product was purified by column chromatography (hexane:ethyl acetate, 1:9).

2.3. General procedure for chalcogenoacetylenes

To a round-bottom flask was added the following: DMSO (2 mL), phenylacetylene (120 mg, 1.0 mmol) the respective diorganoyl dichalcogenide (0.5 mmol), Cs_2CO_3 (650 mg, 1 mmol), selanylpyrazole **2a** (13 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol). The reaction mixture was stirred for 25 min at room temperature. The crude product was diluted with water, extracted with ethyl acetate (3 × 25 mL), dried and purified by column chromatography (hexane:ethyl acetate, 1:99).

2.4. General procedure for sulfides

To a round-bottom flask was added the following: DMSO (2 mL), aryl iodide (1.0 mmol) the respective thiophenol (1.0 mmol), Cs_2CO_3 (650 mg, 1 mmol), selanylpyrazole **2a** (13 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol). The reaction mixture was stirred for 6 h at 110 °C. The crude product was diluted with water, extracted with ethyl acetate (3 × 25 mL), dried and purified by column chromatography (hexane:ethyl acetate, 1:99).

3. Results and discussion

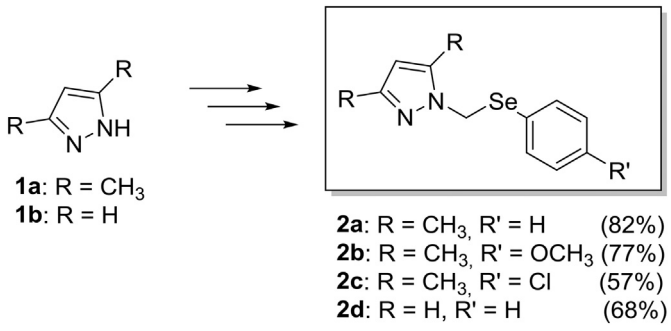
3.1. Synthesis of chalcogenoacetylenes

Thinking of chalcogenoacetylenes as building blocks for more complex structures, the present work arose from the need to access these compounds by a method combining easy preparation, chemoselectivity, and high yields. In this context, we expected that employment of arylselanylpyrazoles as auxiliary ligands could avoid the formation of byproducts, mainly vinylic ones, leading to satisfactory yields associated with short reaction time, low temperature, and aerobic conditions.

The arylselanylpyrazole analogues were readily prepared according to the reference work [23a]. Briefly, starting from pyrazole or 3,5-dimethylpyrazole (**1a** and **1b**), the reaction with paraformaldehyde forms the *N*-substituted aminoalcohol product that is converted to its chlorinated analogue with thionyl chloride. Lastly, the arylselanyl moiety is linked by a nucleophilic reaction between a phenylseleno(trihydro) borate complex, generated in situ from diaryl diselenides and $NaBH_4$, [23b] and a chlorinated alkylpyrazole, leading to the arylselanylpyrazole analogues **2a–d** (Scheme 2).

Reactants: (i) paraformaldehyde (ii) $SOCl_2$, $CHCl_3$ (iii) diphenyl diselenide, $NaBH_4$.

For initial verification of the activity of arylselanylpyrazole-copper complexes in selenoacetylene synthesis, diphenyl diselenide (**3a**) and phenylacetylene (**4a**) were reacted in the presence of a catalyst under aerobic conditions, achieving 60% yield of phenyl(phenylethynyl)selane (**5a**) in a homogeneous catalytic system. The results and reaction parameters are summarized in Table 1. In the initial experiment, the reaction was monitored for 60 min (Table 1, entries 1–4), and it could be observed that product **5a** was formed at a fast rate in the initial minutes. When the reaction was conducted for a prolonged time, subproduct **6** was formed by a second step of arylselanyl coupling.



Scheme 2. Arylselanylpyrazole ligands of copper complexes.

As expected, the model reaction did not occur in the absence of copper and presented only 14% yield when the reaction was performed without ligand (Table 1, entry 6). Reducing the temperature to 25 °C decreased the yield to 30%, and only the selenoacetylene **5a** was selectively generated. Raising the temperature to 80 °C increased the yield moderately to 67%, and at 115 °C an inversion of selectivity occurred.

The catalyst load (2 and 10 mol%) was also investigated (entries 10 and 11, Table 1); it negatively affected the yield at 2 mol% and selectivity at 10 mol%. Among the solvents (entries 12–15, Table 1) and bases (entries 16–18, Table 1) tested, Cs_2CO_3 and DMSO achieved the best results. Note that the use of potassium hydroxide as a base resulted in 55% of solely the selenoacetylene **5a,** while use of DMF favoured the formation of **6**. For the reactions with dichloromethane and toluene as solvent, no product was obtained.

Structural variations of the arylselanylpyrazole ligands reveal that the ligand environment, i.e., the substituents on the arylselanyl and pyrazolyl moieties, influences the catalytic performance of the reaction. The presence of methyl groups at the 3- and 5- positions of the pyrazolyl ring in **2a–c** generates a more active catalytic system (entries 8, 19 and 20, Table 1) compared to **2d** (entry 21, Table 1). This observation can be associated with the greater electron-donating ability of the pyrazolyl unit in **2a–c**, which promotes better stabilization of the catalytically active species, and thus improves the catalytic performance of the reaction.

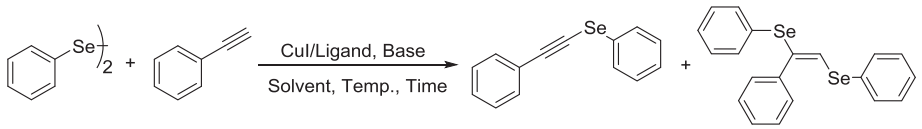
On the other hand, the presence of a methoxy group at the para-position of the arylselanyl moiety in ligand **2b** leads to a small increase in selectivity, while the presence of the electron-withdrawing group chlorine in the arylselanyl moiety of **2c** decreases the formation of **5a**. Despite the small increase in yield obtained with ligand **2b**, we kept using ligand **2a** because it was easier to prepare.

Looking at entries 7 and 16 (Table 1) that showed excellent selectivity, two additional time investigations were done with the respective conditions. While the reaction with potassium hydroxide at 80 °C showed formation of product **6** after 15 min of reaction, the reaction with caesium carbonate at room temperature (entry 22, Table 1) achieved 84% yield in 25 min without the formation of subproduct **6**. Thereby, the optimal reaction conditions were as follows: phenylacetylene (0.5 mmol), diphenyl diselenide (0.5 mmol), CuI (5 mol%), ligand 3 (5 mol%) and Cs_2CO_3 (0.5 mmol) stirred in DMSO for 25 min at 25 °C.

The versatility of this method was established by carrying out several reactions under the optimized reaction conditions with a series of aromatic and aliphatic diselenides (**3a–i**) and terminal alkynes (**4a–g**) (Table 2). Either diphenyl diselenide (**3a**) or phenylacetylene (**4a**) can be replaced successfully with other derivatives highlighting arylacetylenes containing different substituents such as nitro (**4n**), amino (**4o**) and aliphatic (**4j**) and also aliphatic diselenides (**4 g**), besides sulfur and tellurium examples of chalcogenoacetylenes (**4 h** and **4i**) affording the desired products **5a–o**.

In all cases, the reaction is chemically efficient (only formation of **5**), albeit there are differences in yields observed between the different products (from 14% to 88% yield) arising from the difficulty in solubilizing diselenides. The lower yield of the series for **5f** (14%) is attributed to poor solubility of the respective diselenide in the reaction media. Reaction conditions were not changed to evaluate method efficiency according to substituent variation. Furthermore, an increase in temperature, which would circumvent the solubility limitations, promotes formation of subproduct **6**, as was observed in the optimization reactions (Table 1). Despite this limited drawback, the process allows the rapid preparation of a wide array of structurally interesting chalcogenoacetylene compounds.

Table 1
Optimization conditions for CuI/L-catalysed C–Se coupling reaction.[a]



3a **4a** **5a** **6**

#	Cat. (mol%)	L	Base	Solvent	t^b	T (°C)	Yield (%) 5:6
1	CuI (5)	**2a**	Cs_2CO_3	DMSO	7	60	69 (87:13)
2	CuI (5)	**2a**	Cs_2CO_3	DMSO	15	60	91 (50:50)
3	CuI (5)	**2a**	Cs_2CO_3	DMSO	30	60	94 (30:70)
4	CuI (5)	**2a**	Cs_2CO_3	DMSO	60	60	98(28:72)
5	–	**2a**	Cs_2CO_3	DMSO	7	60	–
6	CuI (5)	–	Cs_2CO_3	DMSO	7	60	14(100:0)
7	CuI (5)	**2a**	Cs_2CO_3	DMSO	7	25	30(100:0)
8	CuI (5)	**2a**	Cs_2CO_3	DMSO	7	80	78 (85:15)
9	CuI (5)	**2a**	Cs_2CO_3	DMSO	7	115	95(28:72)
10	CuI (2)	**2a**	Cs_2CO_3	DMSO	7	80	39 (90:10)
11	CuI (10)	**2a**	Cs_2CO_3	DMSO	7	80	93 (65:35)
12	CuI (5)	**2a**	Cs_2CO_3	DMF	7	80	93 (52:48)
13	CuI (5)	**2a**	Cs_2CO_3	CH_2Cl_2	7	80	2 (0:100)
14	CuI (5)	**2a**	Cs_2CO_3	Tol.	7	80	–
15	CuI (5)	**2a**	Cs_2CO_3	MeCN	7	80	28 (0:100)
16	CuI (5)	**2a**	KOH	DMSO	7	80	55(100:0)
17	CuI (5)	**2a**	$N(Et)_3$	DMSO	7	80	7(100:0)
18	CuI (5)	**2a**	NaOMe	DMSO	7	80	23(100:0)
19	CuI (5)	**2b**	Cs_2CO_3	DMSO	7	80	80 (87:13)
20	CuI (5)	**2c**	Cs_2CO_3	DMSO	7	80	76 (47:53)
21	CuI (5)	**2d**	Cs_2CO_3	DMSO	7	80	33 (73:27)
22	CuI (5)	**2a**	Cs_2CO_3	DMSO	25	25	84(100:0)

[a] Reaction conditions: phenylacetylene (1.0 mmol), diphenyl diselenide (1.0 mmol), base (1.0 mmol) and solvent (2 mL). [b] minutes.

3.2. Mechanism investigation

In order to propose a plausible mechanism for selenoacetylene synthesis, ESI-HRMS and ^{77}Se NMR experiments were carried out. In ^{77}Se NMR spectra, the resonance at 463 ppm refers to the reference signal (diphenyl diselenide). The proposed catalytic cycle for the acquisition of **5a** by using **2a**/CuI as catalyst is shown in Scheme 3. Formation of the arylselanylpyrazole–copper complex $[Cu(N_{Pz}\text{-}Se_{Ar})]^+$ (**7**) was confirmed by ESI-HRMS and ^{77}Se NMR analysis. In a first set of experiments, 1 equivalent of **2a** was reacted with 1 equivalent of CuI in THF at 25 °C for 15 min. The molecular ion peak observed at m/z = 329.0946 in the mass spectrum is in agreement with the formation of the copper complex **7** (calc. For $C_{12}H_{14}CuN_2Se$ = 328.9618) (Fig. 1, Supporting Information). The ^{77}Se NMR spectrum of the reaction also corroborates the formation of **7**. Actually, the ^{77}Se NMR spectrum of the complex (Fig. 3b, Supporting Information) presents one signal at 406.1 ppm, which was shifted to a low chemical frequency by about 12 ppm compared to that found for ligand **2a** (417.8 ppm). The observed low-frequency shift with respect to the peak of the free ligand in the ^{77}Se NMR spectrum indicates that the Se atom is coordinated to the Cu centre. The low-frequency shifts in the group 16-coordinated copper complexes presumably result from the effect of the electron-rich d^{10} metal centre. This result is consistent with similar findings for copper complexes chelated by selenium or tellurium donor ligands already described in the literature [25].

The initial step in the catalytic cycle occurs by oxidative addition of diphenyl diselenide to copper resulting in the formation of $[(PhSe)_2Cu(N_{Pz}\text{-}Se_{Ar})]^+$ (**8**). Formation of the intermediate **8** was also corroborated by ESI-HRMS and ^{77}Se NMR. In a second experiment, 3 equivalent of $(PhSe)_2$ were reacted with 1 equivalent of **7** in THF at 25 °C for 15 min. Observation of the adduct $[(PhSe)_2Cu(N_{Pz}\text{-}Se_{Ar})(THF)_2]^+$ m/z = 785.0031 (calc. For $C_{32}H_{40}CuN_2O_2Se_3$ = 784.9889) in the mass spectrum for the reaction indicates the formation of **8** in the catalytic cycle (Fig. 2, Supporting Information). This result is also supported by the ^{77}Se NMR experiments (Fig. 3c, Supporting Information). The ^{77}Se NMR spectrum shows three peaks: one at 463.0 ppm corresponding to $(PhSe)_2$, another at 391.6 ppm from the $PhSe^-$ bound to Cu, and the last one at 422.0 ppm corresponding to the arylselanylpyrazole ligand. It is worth mentioning that the selenium signal of the ligand shifts back to higher frequencies (similar to that reported for the free ligand), suggesting that the arylselanylpyrazole ligand acts, in fact, as a hemilabile ligand. These results can be associated with the less pronounced interaction between the Cu and Se atoms, in which the arylselanyl group acts in a hemilabile fashion favouring the oxidative addition of $(PhSe)_2$.

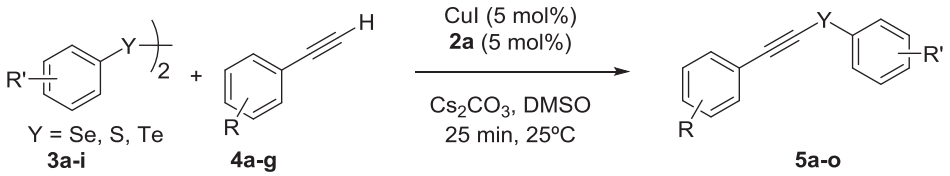
Based on the results of previous work on chalcogenoacetylene preparation via metallic catalysts and related reaction couplings, we propose that in the next step of the catalytic cycle, the terminal alkyne coordinates to the $[(PhSe)_2Cu(N_{Pz}\text{-}Se_{Ar})]^+$ adduct via a π-complex leading to **9**, which is sequentially conducted to **10** with the abstraction of selenophenol. Reductive elimination of the intermediate **10** generates the desired product and regenerates the catalyst. [9,26]

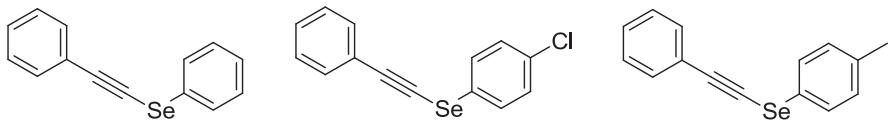
3.3. Synthesis of sulfides

Furthermore, we next explored the generality of the newly defined copper–arylselanylpyrazole system for carbon–sulfur bond formation. The previous optimized conditions were used as the starting point for the new optimization study. Reaction between thiophenol (**11a**) and iodobenzene (**12a**) with 5 mol% of copper–arylselanylpyrazole catalyst (entry 1, Table 3) afforded diphenyl sulfide (**13a**) at 17% yield. In a second set of experiments, a temperature investigation was performed by heating the reaction to 60 and 110 °C (entries 2 and 3, Table 3) achieving, respectively, 48% and 95% yield.

In the absence of copper iodide (entry 4, Table 3), no reaction was observed. When the reaction was carried out without **2a** (only with copper iodide) (entry 5, Table 3), the yield obtained for product **13a** drastically decreased to 24%. As observed for C–Se bond formation, sulfide preparation requires the use of arylselanylpyrazole. These results indicate that these compounds act as auxiliary ligands for copper and play a major role in stabilizing the catalytic active species. Lastly,

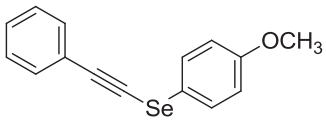
Table 2
Synthesis of chalcogenoacetylenes catalysed by copper–arylselanylpyrazole **2a**[a].

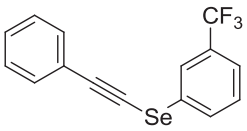


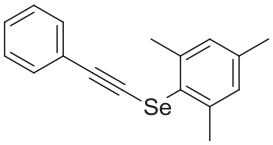

5a (84%)

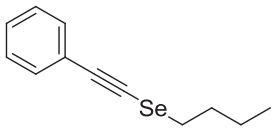
5b (81%)

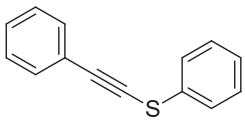
5c (82%)

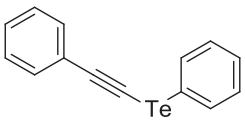

5d (76%)

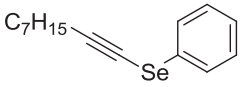

5e (48%)

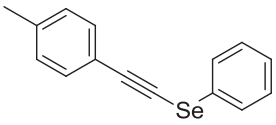

5f (14%)[b]

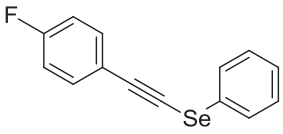

5g (51%)

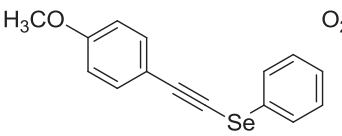

5h (88%)

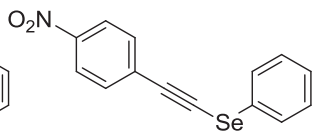

5i (38%)

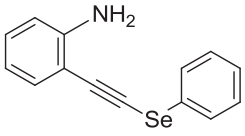

5j (70%)


5k (42%)


5l (60%)


5m (40%)

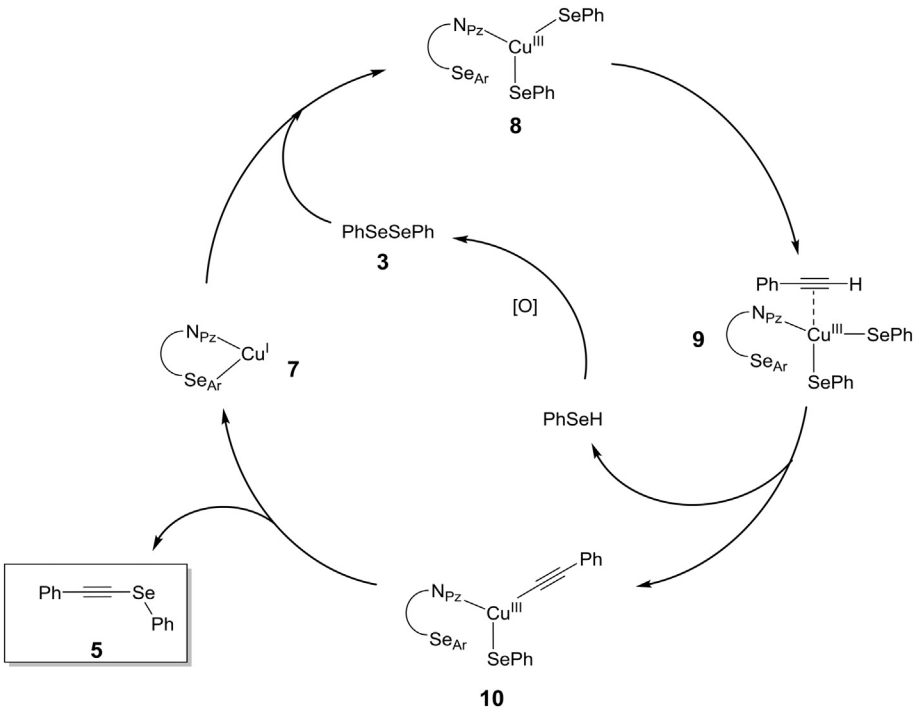

5n (52%)


5o (88%)

a Reaction conditions: acetylene (0.5 mmol), diorganoyl dichalcogenide (0.5 mmol), CuI (5 mol%), ligand **2a** (5 mol%), Cs_2CO_3 (0.5 mmol), DMSO (2 mL), 25 min, 25 °C; [b] GC–MS.

the effect of structural variation of the arylselanylpyrazole on catalytic activity was evaluated, showing a behaviour similar to that of the earlier chalcogenoacetylenes. The presence of methyl groups at the 3- and 5- positions of the pyrazolyl ring in **2a–c** generates a more active and selective catalytic system (entries 3, 6 and 7, Table 3) compared to **2d**, which provided only 37% yield (entry 8, Table 3). In the same way as for chalcogenoacetylenes, the presence of an electron-donating methoxy group at the para-position of the arylselanyl moiety in **2b** was found to give a higher yield (97%), followed by the non-substituted **2a** (95%), and by the electron-withdrawing chloro-substituted **5c** (90%). As the result achieved with ligand **2a** was similar to that with **2b**, we used compound **2a** in the subsequent sequence of work.

With the optimal reaction conditions in hand, we investigated the scope of the aryl iodides and thiols for disulfide preparation (Table 4). Substituted aryl iodides containing electron-withdrawing and donating groups in the para, meta and ortho positions, such as Cl, Br, CF_3, OCH_3, CH_3 and NO_2, all afforded the desired arylation products **13a-m** at moderate to excellent yields. Surprisingly, sterically hindered ortho-substituted aryl iodides afforded the desired products at higher yields in comparison with their para-analogues.



Scheme 3. Proposed mechanism for selenoacetylene synthesis using **2a**/CuI as catalyst.

Moreover, no reaction was observed with ortho-substituted $COOCH_3$, and the para-substituted NH_2 group gave a lower yield. Therefore, it is highlighted that for the amino-containing chalcogenoacetylene **5o**, this behaviour was not pronounced and the reaction yield was 88%.

Notably, it was possible to prepare derivatives with a nitro moiety, with a quantitative yield, and substitution with thiophenol also afforded the desired products with moderate yield. One example of a non-symmetrical diorganoselenide was synthesized from 4-iodonitrobenzene and diphenyl diselenide, evidencing that copper-selanylpyrazole is a promising catalyst for this reaction.

4. Conclusions

In summary, we have designed a versatile organocatalyst based on copper and selanylpyrazole ligands to promote carbon–sulfur and carbon–selenium bond formation. This catalyst was applied to obtain chalcogenoacetylenes from acetylenes and diorganoyl diselenide, and it was extended to prepare sulfides from aryl halides and thiols with moderate to excellent yields. The proposed catalyst presents broad functional-group tolerance including amino, nitro and alkyl substituents, combined with good selectivity, mainly for chalcogenoacetylenes. This efficient and easy-to-perform protocol can be handled under aerobic conditions in a short reaction time. With these results in hand, the next step will be to evaluate carbon-carbon bond formation reactions employing chalcogenoactylenes and *bis*-arylselanyl olefins as starting materials.

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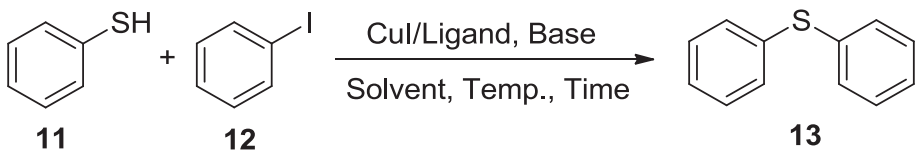
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://

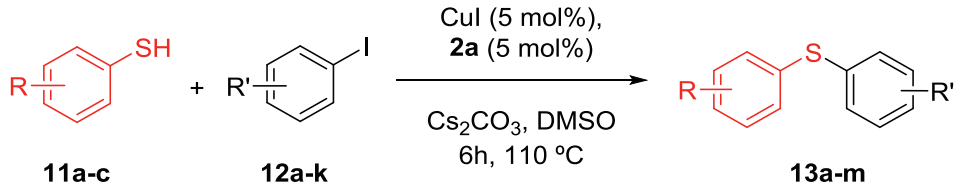
Table 3
Optimization of reaction conditions for CuI/**2a-d** catalysed C−S coupling reaction.



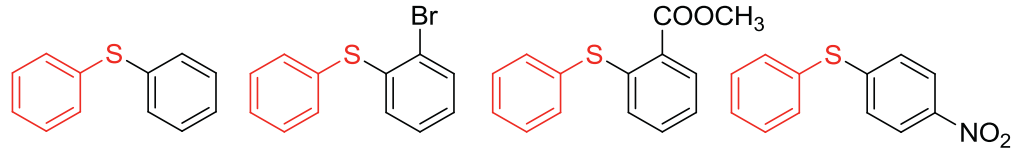
#	Catalyst (mol%)	L	Base	Solvent	*t* (h)	T (°C)	Yield[a] (%)
1	CuI (5)	**2a**	Cs_2CO_3	DMSO	6	25	17
2	CuI (5)	**2a**	Cs_2CO_3	DMSO	6	60	48
3	CuI (5)	**2a**	Cs_2CO_3	DMSO	6	110	95
4	–	**2a**	Cs_2CO_3	DMSO	6	110	–
5	CuI (5)	**–**	Cs_2CO_3	DMSO	6	110	24
6	CuI (5)	**2b**	Cs_2CO_3	DMSO	6	110	97
7	CuI (5)	**2c**	Cs_2CO_3	DMSO	6	110	90
8	CuI (5)	**2d**	Cs_2CO_3	DMSO	6	110	37

[a] Isolated Yields.

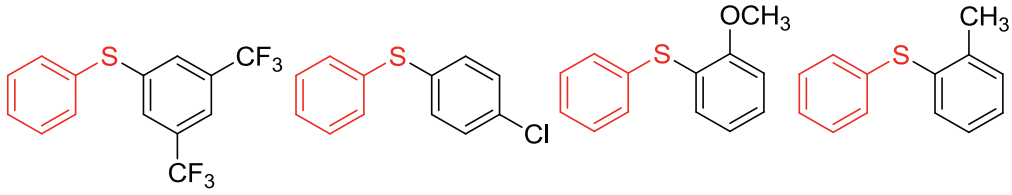
Table 4
Synthesis of sulfides catalysed by copper–arylselanylpyrazole.[a]



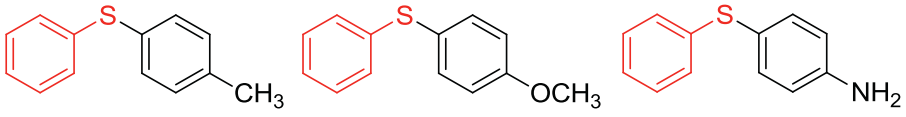
11a-c **12a-k** **13a-m**



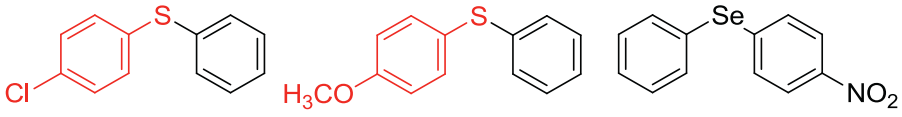
13a (95%) **13b** (95%) **13c**[b] **13d** (99%)



13e (72%) **13f** (30%) **13g** (59%) **13h** (95%)



13i (81%) **13j** (38%) **13k** (24%)



13l (55%) **13m** (40%) **14** (37%)

a Isolated yields after column chromatography. [b] No product obtained.

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