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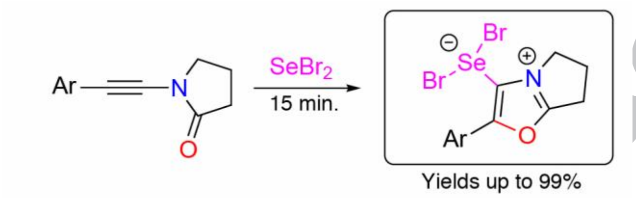

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Addition of selenium(II) bromide to arylalkynylamides – a route to hypervalent T-shaped 10–Se–3 systems

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ABSTRACT

A route for the generation of hypervalent T–shaped 10-Se-3 systems is described involving an interaction between *in situ* prepared selenium(II) bromide and an aryl alkynyl amide derivative. The existence of hypervalent selenium in both the solid and solution states has been supported by X-ray analysis and ^{77}Se NMR data.

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Selenium is able to form highly versatile organic and inorganic hypervalent compounds due to its wide range of oxidative states and its unoccupied valence d orbitals.[1] Trivalent selenium compounds bearing a formal positive charge on the selenium atom have been extensively described,[1] but much less is known about the negatively charged T-shaped trivalent selenium groups. These type of compounds, which feature a linear X–Se–X or X–Se–Y moiety (X = Cl, Br, I; Y = CN), are frequently designated as a 10–Se–3 system, which means that 10 electrons are associated with the central selenium atom but only six (3 pairs) are involved in bonding.[2] The most widely used method for the formation of T-shaped selenium moieties containing a C–Se bond involve an oxidative addition of halogens (Cl_2,[3] Br_2,[3a,c,4] I_2[3a,c,4a,5]), interhalogens (IBr),[6] or pseudohalogens (ICN)[7] to the selenium atom of the corresponding selone derivative. However, generation of such a system has also been accomplished by the addition of selenium halides to an *N*-heterocyclic carbene[8] or by reaction of diaryldiselenide derivatives with an excessive amount of the corresponding dihalogen.[9] Herein, we report an alternative method for the synthesis of a new type of oxazolinium derived hypervalent T-shaped 10–Se–3 system utilizing the addition of selenium(II) bromide to the triple bond of the corresponding *N*-aryl(hetaryl)alkynyl pyrrolidinone.

As the selenohalogenation of aryl(thienyl)alkynes[10] is one of the most straightforward synthetic pathways for the preparation of benzo[*b*]selenophenes and selenophenothiophenes, we were inspired to further expand the existing protocol. Because almost nothing was known about the selenohalogenation of aryl alkyne derivatives bearing heteroatoms directly attached to the triple bond, we decided to pursue this research direction. Aryl alkynyl amides were found to be suitable substrates for this investigation due to their stability and relatively simple preparation. The initial alkynyl amides **3a-g** were prepared by a two-step procedure (Scheme 1). Benzaldehydes **1a-f** and thiophene-2-carbaldehyde (**1g**) were converted to the corresponding dibromovinylbenzenes(thiophene) **2a-g** by the Corey–Fuchs[11] protocol. Subsequent CuI/DMEDA (*N,N'*-dimethylethylenediamine) catalyzed coupling[12] of **2a-g** with pyrrolidin-2-one led to the desired alkynyl amides **3a-g**. Next, alkynyl amides **3a-g** were treated with *in situ* prepared selenium(II) bromide[13] in $CHCl_3$. Unexpectedly, the reaction of phenylethynyl amide **3a** with $SeBr_2$ failed to yield the corresponding 3-bromobenzo[*b*]selenophene derivative, instead generating a new type of 10–Se–3 system **4a**. Since selenirenium species have been widely[14] postulated as the key intermediates in reactions of selenium electrophiles with C≡C triple bonds, we propose that the reaction begins with the coordination of $SeBr_2$ to the triple bond of **3a**, forming selenirenium type adduct **A**, which induces an intramolecular nucleophilic attack of oxygen onto the carbon of the triple bond to form a five-membered cycle. The intramolecular nucleophilic attack of the carbonyl oxygen seems to be favored over the expected selenobromination. Product **4a** began to precipitate as a yellow amorphous solid during the addition of alkynyl amide **3a** to the selenium(II) bromide solution. Complete consumption of the starting material was observed in 15 min (TLC), then the reaction was left to stir overnight to achieve complete precipitation of the product, which was isolated in 50 % yield after filtration. In a similar manner, a series of hypervalent selenium compounds **4b-g** were prepared in moderate to high yields. It was concluded that electron-rich substrates were generally more suitable for these reactions, thus enabling the desired products to be obtained in higher yields.

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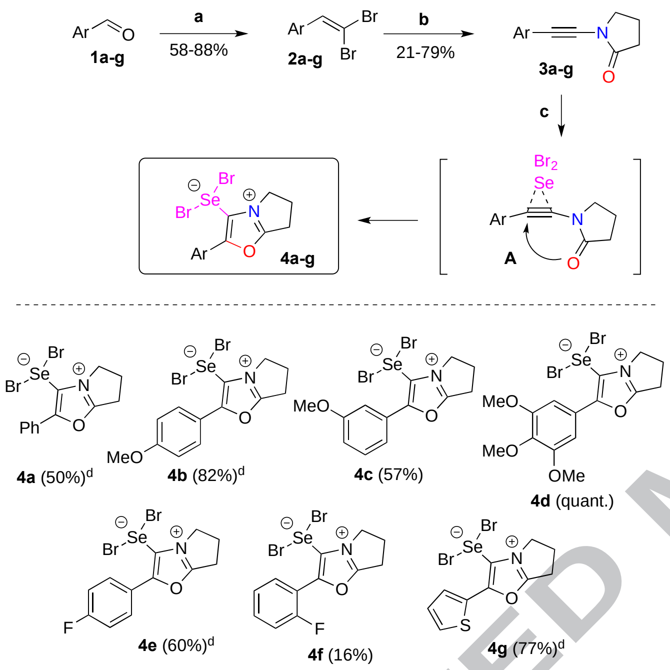
This was exemplified by the low yield obtained for *o*-fluorosubstituted **3f** and quantitative yield using trimethoxy substituted **3d**. A modified isolation procedure was required to obtain **4c**, **d**, **f** as these products did not precipitate directly from the reaction mixture, even after stirring for 24 h. Thus, the reaction mixture was evaporated under reduced pressure after stirring for 15 min at 0 °C, and the corresponding product was successfully precipitated by stirring in a mixture of petroleum ether and $CHCl_3$. The modified procedure also worked well for the other products, but highly pure compounds were more easily obtained by direct precipitation from the reaction mixture. To the best of our knowledge, this is a new route for preparation of zwitterionic T-shaped trivalent selenium derivatives.



Scheme 1. Synthetic procedure for the preparation of hypervalent T-shaped compounds **4a-g**. (a) **1a-g** (1.0 equiv.), CBr_4 (1.5 equiv.), PPh_3 (3.0 equiv.), CH_2Cl_2, 0 °C, 2 h; (b) **2a-g** (1.0 equiv.), pyrrolidin-2-one (1.0 equiv.), CuI (12 mol%), DMEDA (18 mol%), Cs_2CO_3 (4.0 equiv.), dioxane, 60 °C, 24 h; (c) **3a-g** (1.0 equiv.), $SeBr_2$ (1.0 equiv.), $CHCl_3$, 0 °C, 15 min. ^{d} To achieve complete precipitation of the corresponding products **4a, b, e, g** the reaction mixture was stirred at room temperature for an additional 24 h.

The chemical shift values in the ^{77}Se NMR spectra for known analogous trivalent systems are found in the range of approximately 300 to 400 ppm,[3a,4b,c] showing considerably higher shielding than in the case of the corresponding divalent PhSeBr system (888 ppm in dioxane). The ^{77}Se chemical shifts for the new derivatives **4a-g** ranged from 344 ppm for **4g** to 374 ppm for **4d**. These results suggest the hypervalent state of selenium in solution. Compounds **4a-g** were relatively stable and could be stored in a closed system at room temperature for several months without any signs of decomposition, however, the slow appearance of red selenium was observed in the presence of air. These compounds are insoluble in nonpolar organic solvents but slightly soluble in acetonitrile and acetone. In highly polar solvents (DMSO, DMF, and water), these substances quickly decompose which was accompanied by the precipitation of amorphous selenium. Because of their thermal instability, no melting points were obtained. In general, upon heating above 100 °C, compounds **4a-g** decompose, as evidenced by a color change.

The structures of **4a, b, e, g** were unambiguously confirmed by X-ray analysis (Figure 1). Monocrystals of **4a** were obtained by crystallization from an oversaturated solution in acetone, but in the cases of **4b, e, g,** acetonitrile was used as a solvent. In the crystal structures of **4a** and **4g,** strong intermolecular σ-hole interactions between the T-shaped selenium atom and the bromine of another molecule were observed. By means of these interactions, centrosymmetric molecular pseudodimers containing square-planar coordinated selenium atoms were formed. The corresponding intermolecular Se$\cdots$Br distances are equal to 3.4439(8) Å and 3.3374(5) Å for **4a** and **4g**, respectively. A perspective view of the molecular pseudodimer of the thiophene derivative **4g** is illustrated in Figure 1A. Similar centrosymmetric pseudodimers formed by Se$\cdots$Br σ-hole interactions have also been observed in previously reported crystal structures;[15] however, the same interactions were weaker, and their lengths fell in the range of 3.491-3.610 Å. Unlike the crystal structures of phenyl derivative **4a** and thienyl analogue **4g** (Figure 1A), the Se$\cdots$Br σ-hole interactions in 4-fluorophenyl substituted **4e** did not lead to the formation of analogous centrosymmetric pseudodimers (Figure 1B). Because of the elevated electronegativity of C-5, strong intermolecular CH$\cdots$F type hydrogen bonds are present, leading to the formation of molecular chains along the screw axes 2_1 parallel to the lattice parameter ***a*** (space group is *Pbca*). In this case, the distance of the intermolecular Se$\cdots$Br interaction is 3.556(1) Å, and the length of the hydrogen bonds is 2.948(9) Å. A similar type of packing for the 10-Se-3 system has been shown by Mugesh[4a] and co-workers in the crystal structure of dibromo(1-methyl-3-benzylimidazolium-2-yl)selenide. This compound forms molecular chains along the screw axes 2_1 parallel to the lattice parameter ***b*** (space group *Pbca*) supported by the corresponding Se$\cdots$Br σ-hole interactions with a distance equal to 3.507(1) Å.

In contrast to the crystal structures of **4a**, **4e**, and **4g**, no shortened intermolecular Se$\cdots$Br contacts were found in the crystal structure of **4b**. Instead, the selenium atom formed a moderate intermolecular Se$\cdots$O σ-hole bond (3.232(5) Å) with the oxygen atom of the methoxy group, which leads to the continuation of molecular chains along the crystallographic direction [101] (Figure 1C). As a result, similar to 4-fluorophenyl substituted **4e**, no centrosymmetric pseudodimers were observed in the crystal structure of 4-methoxyphenyl derivative **4b**. Considering that the crystal structure of **4b** belongs to space group *Pn*, non-centrosymmetric physical properties described by third-rank tensors (piezoelectricity, second harmonic generation, *etc.*) could be expressed. Due to their symmetry, all components of the third-rank tensors for centrosymmetric crystals are zero.[16] The main geometric parameters characterizing the square-planar coordination of selenium in compounds **4a**, **4e**, and **4g** are listed in Table 1. It should be noted that the length of the Se$\cdots$Br σ-hole interaction in thienyl derivative **4g** is the shortest among all known hypervalent T-shaped 10-Se-3 systems. However, it seems that the nature of the substituent has a slight influence on the σ-hole interaction length. This length is most strongly affected by the crystal packing effect and temperature.[17] The packing coefficients for **4a**, **4b**, **4e**, and **4g** were calculated based on Kitaigorodsky's[18] approach (Table 1). A consistent correlation between the packing coefficient and the length of the Se$\cdots$Br σ-hole interaction in **4a**, **4b**, and **4g** was observed, meaning that denser crystal structures yield weaker intermolecular interactions. In the structures studied, the atomic lines Br15−Se14−Br16 have considerable angles with the oxazolinium plane. Overall, the tricyclic systems in the molecular structures are nearly planar; the carbon atom of C6 insignificantly deviates from the oxazolinium planes. The dihedral angles between the aryl rings and the oxazolinium planes are as follows: 1.6(4)° (**4a**), 14.4(5)° (**4b**),

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25.1(5)° (**4e**) and 4.4(3)° (**4f**). It should be noted that the crystal structure **4f** features static disorder in the thienyl group.

An alternative method for the generation of zwitterionic hypervalent T–shaped 10-Se-3 systems *via* the treatment of *N*-ethynylpyrrolidinones with $SeBr_2$ in moderate to high yields has been described. The existence of hypervalent selenium in both the solid state and solution has been unambiguously confirmed by X-ray analysis and ^{77}Se NMR data. Future research dedicated to studying the reactions of aryl alkynyl amides with other selenium halides and the use of other aryl alkynyl derivatives containing heteroatoms directly attached to the triple bond is in progress.

Supporting Information

Supporting information containing full experimental data, copies of the ^1H, ^{19}F, and ^{13}C NMR spectra of all compounds, and crystallographic data for compounds **4a**, **4b**, **4e** and **4g**[19] can be found, in the online version, at http://dx.doi.org/

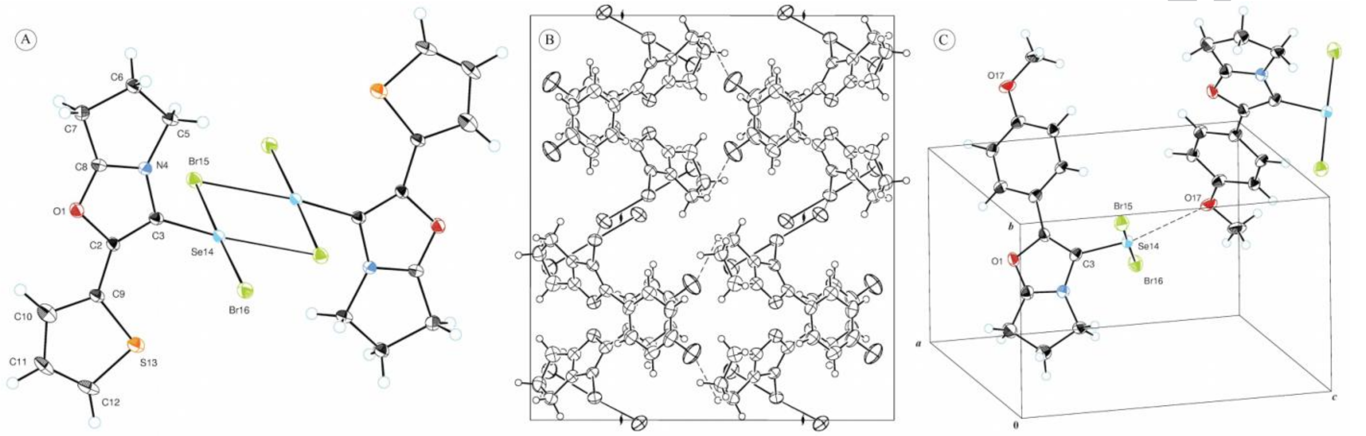

Figure 1. A: view of molecular pseudodimers formed by **4g**, showing the atom-numbering scheme; B: projection of the crystal structure of **4e** along crystallographic direction [100], showing the screw axes of second order, unit cell outlines, σ-hole and hydrogen bonds; C: Partial crystal structure of **4b**, showing the formation of a σ-hole interaction and unit cell outlines. Displacement ellipsoids are drawn at 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 1. Geometrical parameters of square-planar coordinated selenium in **4a, 4b, 4e,** and **4g**

	4a	**4b**	**4e**	**4g**
C3−Se14, Å	1.906(3)	1.904(5)	1.870(5)	1.894(3)
Se14−Br15, Å	2.6356(8)	2.534(1)	2.586(1)	2.6199(5)
Se14−Br16, Å	2.5569(8)	2.637(1)	2.600(1)	2.5724(5)
Se14···Br15, Å	3.4439(8)	3.232(5)[a]	3.556(1)	3.3374(5)
C3−Se14···Br15#1,°	173.5(1)	164.4(3)[b]	156.6(2)	168.5(1)
Br15−Se14−Br16,°	63.2(1)	85.1(2)	81.9(2)	65.6(1)
C6 deviation, Å	0.152(5)	0.244(6)	0.070(5)	0.256(4)
Packing coefficient	0.713	0.709	0.677	0.736

[a] Se14···O17 σ-hole bond length; [b] C3−Se14···O17 angle.

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