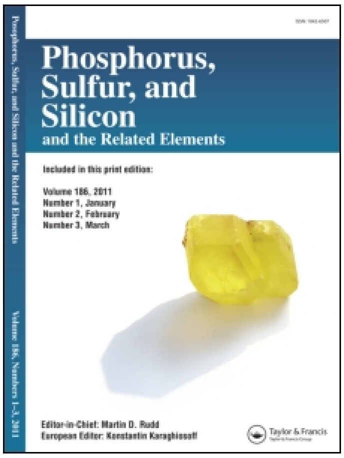

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Synthetic Methods of Selenium- and Tellurium Variants of Tetrathiafulvalene Electron Donors

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Synthetic Methods of Selenium- and Tellurium Variants of Tetrathiafulvalene Electron Donors

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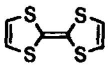
Two very useful, versatile reactions applicable to the synthesis of TTF-type electron donors are presented: the one-pot preparation of 1,3-dichalcogenole-2-chalcogenones from readily available terminal alkynes and the ready formation of heterocyclic rings fused on TTF by transalkylation on a chalcogen atom. These reactions in combination with a conventional trialkyl phosphite-promoted coupling reaction of 1,3-dichalcogenole-2-chalcogenones provide a ready access to novel selenium- and tellurium- variants of TTF-type electron donors. A variety of synthetic examples of these compounds, especially inaccessible ones of six-membered heterocycle-fused type, five-membered heterocycle-fused type, dimeric type, and cyclophane type, are demonstrated.

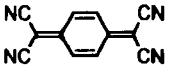
Keywords: organic conductor; electron donor; molecular complex; heterocycle

INTRODUCTION

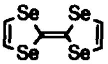
Since the molecular complex of tetrathiafulvalene (**1**, TTF) and tetracyanoquinodimethane (**2**, TCNQ) gave the first organic metal, the development of novel TTF-type electron donors has been actively carried out.[1] As a result, a great number of TTF derivatives and their highly conductive molecular complexes have been reported.[2] In the molecular designs of superior TTF-type electron donors, two principal guidelines are proposed: replacement of the sulfur atoms of the TTF skeleton by selenium or tellurium atoms and annelation of additional heterocycle rings. According to the first guideline, tetraselenafulvalene (**3**, TSF)[3] and tetratellurafulvalene (**4**, TTeF)[4] were developed, and the introduced heavy chalcogen atoms can greatly contribute to strengthening of intermolecular contacts, which thus lead to enhancement of the dimensionality of donor assembly in molecular complexes and stabilization of metallic states at low-temperatures.[5] Further study along this guideline led to the discovery of the first organic superconductor based on tetramethyltetraselenafulvalene (**5**, TMTSF).[6]



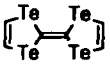
1 (TTF)



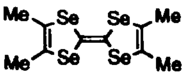
2 (TCNQ)



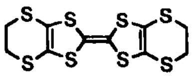
3 (TSF)



4 (TTeF)



5 (TMTSF)

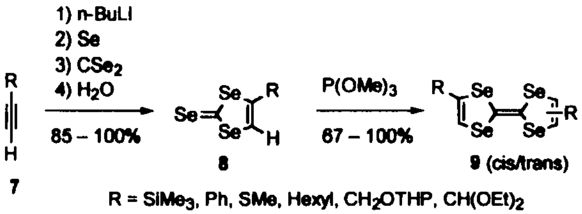


6 (BEDT-TTF)

According to the second guideline, bis(ethylenedithio) tetrathiafulvalene (6, BEDT-TTF) was developed, where the increasing number of the chalcogen atoms can also strengthen intermolecular contacts, resulting in the discovery of many organic superconductors based on BEDT-TTF, which include those of κ-type with Tc > 10 K.[7] Although much effort has been still continued along these guidelines, it is generally difficult to synthesize selenium- and tellurium-containing TTF electron donors, especially of heterocycle-fused type, and only a few of limited synthetic methods have been developed so far. Here we would like to present very useful and versatile reactions that are conveniently applicable to the syntheses of selenium- or tellurium-variants of TTF type electron donors and demonstrate a number of practical application examples.

1. ONE-POT PREPARATION OF 1,3-DICHALCOGENOLE-2-CHALCOGENONES

In the synthesis of TTF and TSF derivatives, key intermediates are 1,3-dichalcogenole-2-chalcogenones, but those with versatile and



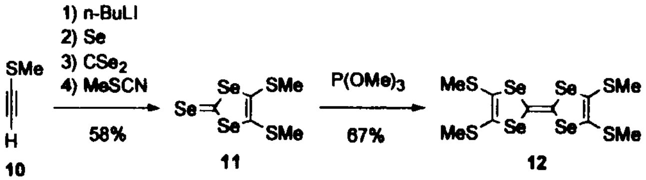
R = $SiMe_3$, Ph, SMe, Hexyl, CH_2OTHP, $CH(OEt)_2$

SCHEME 1

convertible functional groups are rather inaccessible.[2] Mayer and co-workers in 1964 reported a simple synthesis of 1,3-dithiole-2-thione by cyclization reaction of sodium acetylides with sulfur and carbon disulfide in liquid ammonia.[8] The yield was, however, very low (25%). Later this method was also applied to the preparation of 1,3-diselenole-2-selone in a low yield (15–25 %).[3] We recognized that, in spite of the disadvantages of its low yield and laborious procedure using liquid ammonia as well as use of toxic carbon diselenide for the selenium case, this reaction has a significant potential for a ready access to a variety of 1,3-dichalcogenole-2-chalcogenone derivatives. Our detailed examination of the experimental conditions led to a satisfactory modification:[9] the terminal alkyne (7) with n-BuLi in THF containing TMEDA at –78 °C were converted into lithium acetylides, which were subsequently reacted with selenium at 0 °C for 2 h, then with carbon diselenide at -90 °C for 3 min, and finally quenched with water to give the corresponding 1,3-diselenole-2-selone derivatives (8) in 81–100% (Scheme 1). A similar one-pot reaction using a combination of sulfur and carbon disulfide also gave 1,3-dithiole-2-thiones.

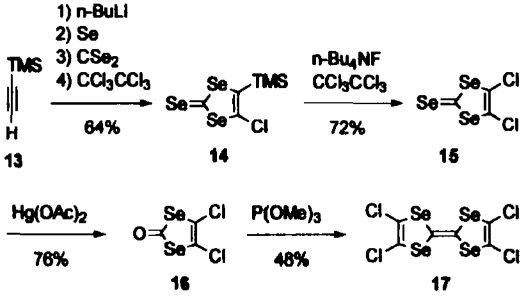
1,3-Dichalcogenole-2-chalcogenones bearing various functional groups can be thus readily obtained, and on dimeric coupling with a trivalent phosphorus reagent, converted to the disubstituted TSF electron donors (9), which usually comprise *cis* and *trans* isomers. Some of the introduced functional groups are versatile and convertible. For example, the trimethylsilyl group can be substituted by hydrogen and halo groups under basic conditions. The tetrahydropyranyloxymethyl and diethoxymethyl groups undergo ready hydrolysis to the hydroxymethyl and formyl groups, respectively, which serve as an important anchor for the synthesis of functionalized TTF systems.

For the synthesis of disubstituted 1,3-diselenole-2-selones, introduction of an additional substituent group is required, which can be done by quenching the successive one-pot reaction of the terminal alkyne with an appropriate electrophile instead of water.[10] For example, when a reaction mixture from methylthioacetylene (**10**) was quenched with excess methyl thiocyanate, 4,5-bis(methylthio)-1,3-diselenole-2-selone (**11**) was obtained in 58% yield and converted to tetrakis(methylthio) TSF (**12**) in 67% yield (Scheme 2).



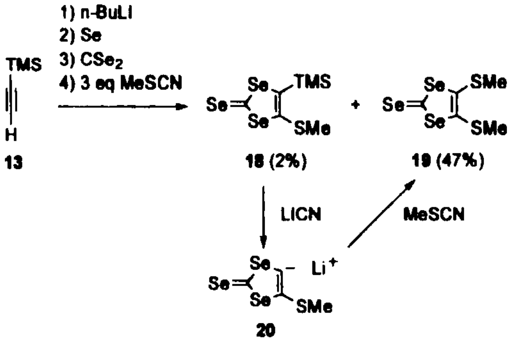
SCHEME 2

A variety of sophisticated tetrasubstituted TSF are thus accessible. Scheme 3 demonstrates the successful synthetic route to tetrachloro TSF (**17**) which is usually difficult to synthesize.[11] The key intermediate **14** is obtained by quenching the one-pot reaction of trimethylsilylacetylene (**10**) with hexachloroethane, and then its trimethylsilyl group can be converted to a chloro group by treatment with tetrabutylammonium fluoride and hexachloroethane. Finally the resulting **15** is converted via the ketone (**16**) to the desired tetrachloro TSF (**17**). It is also possible to prepare the tetrabromo TSF in a similar manner. These halo TSF derivatives are very useful in studying crystal engineering in molecular complexes, where the nonbonded interactions of halo groups are utilized.



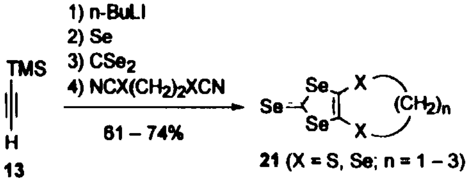
SCHEME 3

We incidentally found that, when a similar one-pot reaction of trimethylsilylacetylene (**13**) was quenched with excess methyl thiocyanate, the 4,5-bis(methylthio) derivative (**19**) was formed (47% yield) instead of the expected 4-methylthio-5-trimethylsilyl derivative (**18**) (2% yield).[10] The formation of **19** is well explained, as shown in Scheme 4: the product (**18**) produced by quenching with methyl thiocyanate further reacts in situ with lithium cyanide concomitantly formed during the quenching to give another intermediate (**20**), which subsequently reacts with an additional methyl thiocyanate, leading to **19**.



SCHEME 4

The above reaction mechanism of bis-methylthiolation provides a short access to the heterocycle-fused 1,3-diselenole-2-selones (**21**).[10] When the reaction mixture of **13** was quenched with one equimolar amount of α,ω-bis(chalcogenocyanato)alkane, a cyclofunctionalization reaction occurred to give the desired **21** in a good yield (Scheme 5). This reaction is widely applicable to the synthesis of a series of 1,3-diselenole-2-selone systems with different methylene numbers, n = 1–3, and different chalcogen elements, S and Se, of the fused heterocyclic ring.

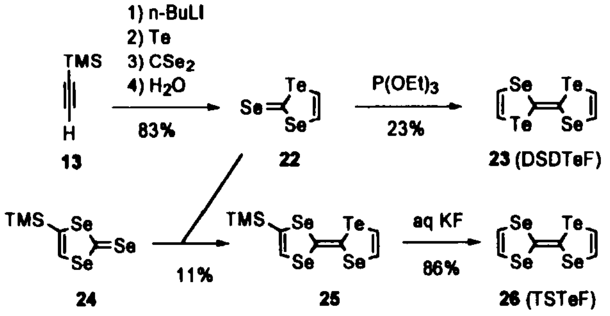


SCHEME 5

2. TELLURIUM-HYBRID TSF ELECTRON DONORS

TTF•TCNQ[1] and TSF•TCNQ[3] complexes demonstrate high room temperature conductivities 500 Scm^{-1} and 800 Scm^{-1}, respectively, but undergo a metal-insulator transition (Peierls transition) at 59 K and 40 K, characteristic of a one-dimensional organic metal. In contrast, TTeF•TCNQ complex shows an extraordinarily high conductivity (2200 Scm^{-1}) and remains metallic down to a measurable low temperature (2 K).[4] Strong nonbonded tellurium-tellurium interactions are responsible for the suppression of the Peierls transition. Compared to TTF and TSF, a disadvantage of TTeF is inaccessibility, and only a limited number of its derivatives have been prepared.

In the one-pot synthetic method, use of different chalcogen kinds for the elemental chalcogen and carbon dichalcogenide reagents can provide a tool for the synthesis of hybrid 1,3-dichalcogenole-2-chalcogenones.[12] Thus 1,3-selenatellurole-2-selone (**22**) was readily obtained in 83% yield by successive treatments of trimethylsilylacetylene (**13**) with 1 eq. n-BuLi, 1 eq. tellurium powder 1 eq. carbon diselenide, and finally water (Scheme 6).[13] Triethyl phosphite-promoted coupling reaction of **22** afforded diselenaditellurafulvalene (**23**, DSDTeF) in 23 % yield. Triselenatellurafulvalene (**26**, TSTeF) was also obtained by a cross-coupling reaction between **22** and **24**, followed by desilylation with aqueous potassium fluoride.[14]

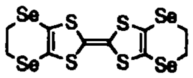


SCHEME 6

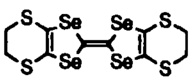
These hybrid compounds not only offer additional examples of tellurium-containing conductive complexes, but also provide useful information on the contribution of the tellurium atoms to the design of organic metals. The conductivity of DSDTeF•TCNQ was very high, 1400 Scm^{-1} which was just in between those of TSF•TCNQ and TTeF•TCNQ. In addition, a variable temperature measurement demonstrated that the conductivity steadily increases to 2.5-fold down to 4 K, and there is no metal-insulator transition, as seen in TTeF•TCNQ. The TSTeF•TCNQ complex showed a further higher conductivity, 2000 Scm^{-1}, but a Peierls transition occurred at 80 K. Evidently replacement of one selenium atom of TSF by tellurium serves to enhance intermolecular interactions enough to induce the high conduction, but replacement of two selenium atoms is required to suppress the Peierls transition.

3. SELENIUM VARIANTS OF BEDT-TTF

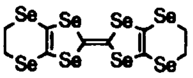
Since the discovery of numerous superconductors based on BEDT-TTF (**6**), extensive efforts have been devoted to its structural modifications.[2] One of the most promising variations is to replace the sulfur atoms of BEDT-TTF with selenium atoms. Symmetrical selenium variants, BEDS-TTF (**27**)[15], BETS (**28**),[16] and BEDS-TSF (**29**)[17] have been already synthesized and utilized for the development of novel metallic radical cation salts. Among them, BETS is especially remarkable because it, like BEDT-TTF, can form superconductors. BETS are, however, generally hard to access and only limited synthetic methods have been known.[18]



27 (BEDS-TTF)

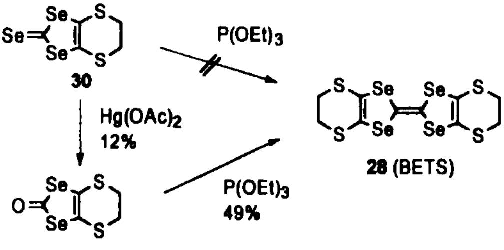


28 (BETS)



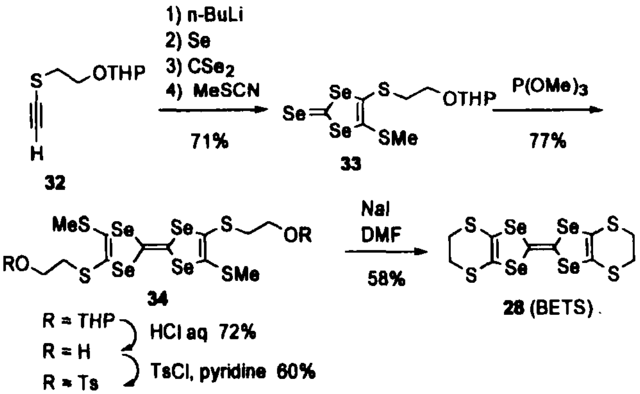
29 (BEDS-TSF)

The readily available ethylenedithio-substituted 1,3-diselenole-2-selone (**30**)[10] was expected to be a promising precursor of BETS, but its direct coupling did not afford BETS because of its thermal instability. Alternatively, **30** was converted to the ketone derivative (**31**), which was then coupled to BETS, but the conversion reaction proceeded only in a low yield (Scheme 7).



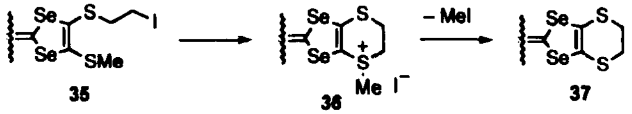
SCHEME 7

The above result prompted us to develop a new synthetic method of BETS and all the possible selenium variants of BEDT-TTF.[19] For this purpose, we devised a combination strategy of (1) one-pot construction of the 1,3-dichalcogenole ring and (2) intramolecular transalkylation on a sulfur atom toward the formation of the outer 6-membered heterocyclic ring, as shown in Scheme 8. Thus, the 1,3-diselenole-2-selone derivative (33) as a key intermediate was first prepared by successive treatments of the THP-protected 2-(ethynylthio)ethanol (32) with butyllithium, selenium, carbon diselenide, and methyl thiocyanate, and then converted to the TSF derivative (34). After deprotection and tosylation, the final heating of the ditosylate with NaI in DMF smoothly gave BETS. All the steps proceed in good to high yields, and thus the present method is superior to the preceding synthetic methods of BETS.[18]



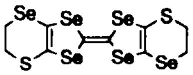
SCHEME 8

The last ring-closure reaction from the iodide intermediate (35) to 37 is very unique, being considered to proceed by an intramolecular transalkylation on a sulfur atom via the sulfonium salt (36) (Scheme 9). The driving force toward the ring cyclization is release of the resulting methyl iodide from the reaction system.

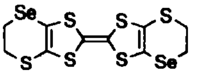


SCHEME 9

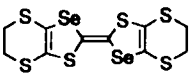
This synthetic method is very versatile and widely applicable to a number of sulfur/selenium hybrid compounds 38 – 43 that are inaccessible by usual synthetic methods.



38 (BEST-TSF)



39 (BEST-TTF)



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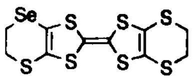

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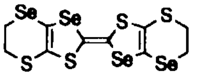

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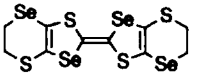
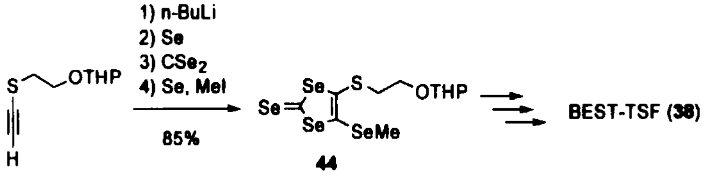


43

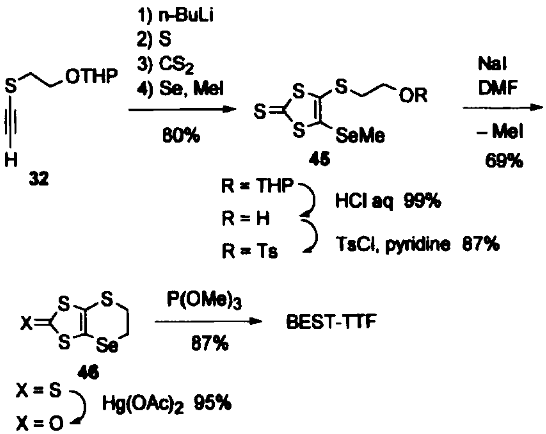
For example, BEST-TSF (**38**) was obtained by a similar reaction sequence via the methylseleno intermediate **44**, where the formation reaction of the fused thiaselenacycloalkane ring occurs through transalkylation on a selenium atom (Scheme 10). On careful comparison, transalkylation on a selenium atom tends to occur in a much shorter time than on a sulfur atom.



SCHEME 10

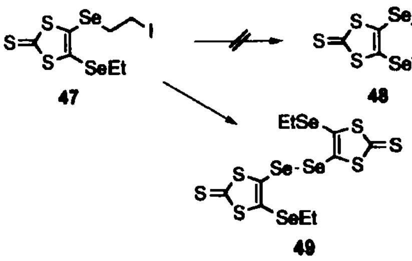
The TTF counterpart, BEST-TTF (**39**) was similarly obtained via **45**, but in the synthesis of TTF series, it turned out that the ring formation from **45** to **46** prior to the conversion to the TTF skeleton is more advantageous (Scheme 11).

The heterocyclic ring formation via transalkylation on a chalcogen atom is very effective for the annelation of additional rings on TTF systems.



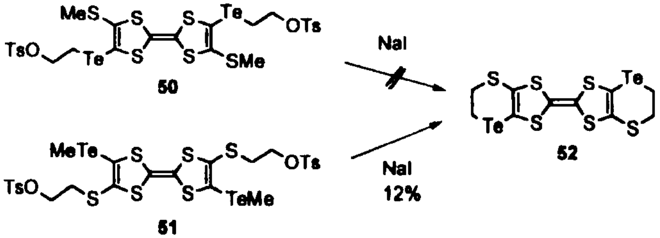
SCHEME 11

However, this method has a limitation on the formation of a diselenacycloalkane ring. When we attempted to prepare the intermediate **48** that is a precursor of BEDS-TTF, we encountered a difficulty in the annelation of the diselenacycloalkane ring from **47** (Scheme 12).[20] The main product was the diselenide **49**, whose formation is considered as follows: the β-selenoethyl iodide is converted via an episelenonium iodide to the selenenyl iodide, which undergoes disproportionation to the diselenide.



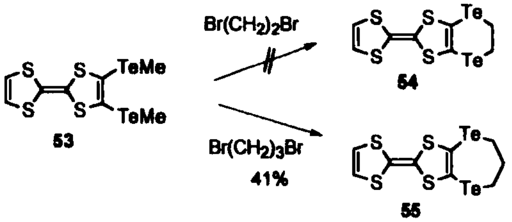
SCHEME 12

Such undesirable decomposition reactions were also observed in the syntheses of tellurium-containing heterocycle fused compounds **52** and **54**. The ditosylate **50** did not give any target compound **52**, presumably because the *in-situ* formed β-telluroethyl iodide preferred decomposition via an epitelluronium iodide to the heteroring formation via transalkylation (Scheme 13).[21] In contrast to this, the reaction of the regioisomer **51** gave **52**, though it was still low in yield and reproducibility.



SCHEME 13

Another unstable example of β-telluroethyl halide was observed in the attempted synthesis of ethyleneditelluro TTF (**54**) via intermolecular transalkylation from bis(methyltelluro)TTF (**53**) and 1,2-dibromoethane (Scheme 14). One may suppose that, after one of the methyltelluro groups is converted to 2-bromoethyltelluro group, a decomposition reaction via an epitelluronium bromide occurs. In contrast, the synthesis of propyleneditelluro TTF (**55**) by the intermolecular transalkylation of **53** and 1,3-dibromopropane smoothly proceeded.[22] In this case, the heteroring formation via the second transalkylation can occur, because the 3-bromopropyltelluro group is stable.

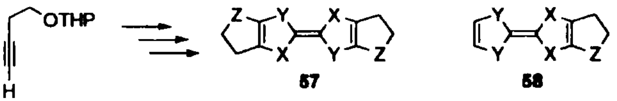


SCHEME 14

4. ETHYLENECHALCOGENO- AND PROPYLENE- CHALCOGENO-TTF-TYPE DONORS

Recently Rovira and coworkers reported that bis(ethylenethio)-tetrathiafulvalene (BET-TTF), early developed by Engler's group,[23] behaves as a superior electron donor.[24] In this connection, we recently developed the selenium variants, which were synthesized from commercially available tetrahydropyranyl (THP)-protected 3-butyn-1-ol (**56**) in a similar manner as described for selenium variants of BEDT-TTF (Scheme 15). Not only all possible selenium variants (**57**) but also unsymmetrical ones (**58**) were obtained by this method.[25]

These donors are characterized by giving highly conductive radical cation salts. In particular, it may be emphasized that the BET-TSF•TCNQ complex and the BES-TSF•TCNQ complex showed extraordinarily high room-temperature conductivities of 2600 and 2700 Scm^{-1}, respectively, which are of the highest class for molecular complexes. The crystal structure of the BES-TSF•TCNQ complex was confirmed to adopt segregated stacking columns. An important feature of this structure is that the donor molecules interact not only with the stacked donor molecules but also with both donor molecules and TCNQ molecules in the neighboring columns. It is thus understandable that the high conductivity of BES-TSF•TCNQ is induced by strong heteroatomic interactions not only along the stacking direction but also along the transverse direction, which are enhanced by the additional outer selenium atoms of BES-TSF.



56

57

X = Y = Z = S (BET-TTF)
X = Y = S, Z = Se (BES-TTF)
X = Y = Se, Z = S (BET-TSF)
X = Y = Z = Se (BES-TSF)
X = Z = S, Y = Se
X = S, Y = Z = Se
X = Se, Y = Z = S
X = Z = Se, Y = S

58

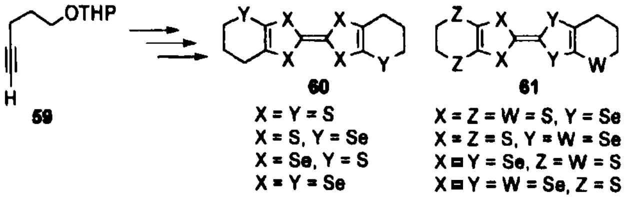
X = Y = S, Z = Se
X = S, Y = Z = Se
X = Y = Z = Se

SCHEME 15

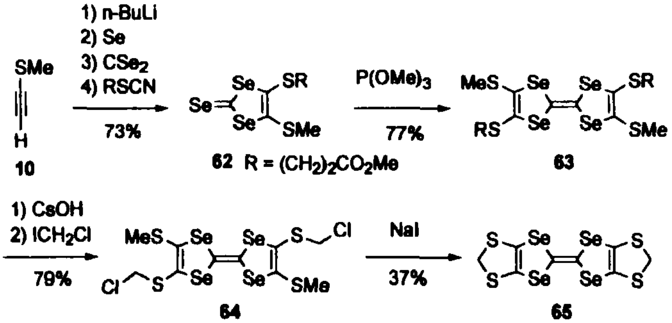
A similar synthetic method using tetrahydropyranyl (THP)-protected 4-propyn-1-ol (**59**) as a starting material was also applied to the synthesis of a series of propylenechalcogeno-substituted TTF-type donors **60** and unsymmetrical similar systems **61** (Scheme 16).[26]

5. METHYLENEDITHIO-TSF DONORS

Another successful example of the present synthetic method is the synthesis of novel bis(methylenedithio)-TSF donor **65**, which is demonstrated in Scheme 17. In this reaction sequence, the synthesis of the precursor 64 is crucial and was accomplished by a strategy based on deprotection/realkylation of the protected TSF dithiolate 63.[27]

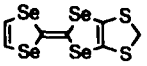


SCHEME 16

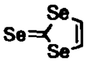


SCHEME 17

An unsymmetrical compound 66 of this type was synthesized by a cross-coupling between 62 and 67 followed by similar heterocyclic ring conversion reactions. This donor is very remarkable not only in that it formed a AuI_2 radical cation salt with a high room temperature conductivity of 2000 Scm^{-1} but also in that the salt became a superconductor below 4.5 K. It should be noticed that the room temperature conductivities of organic superconductors are generally not so high.[7] It was analyzed that the crystal structure has quasi-one dimensional stacking columns of **66**, reminiscent of the Bechgaard salts as the first organic superconductors.[6] A sharp distinction is that the critical temperature (4.5 K) of the present superconducting salt is much higher than that (1.4 K) of the typical Bechgaard superconductor $(TMTSF)_2ClO_4$.



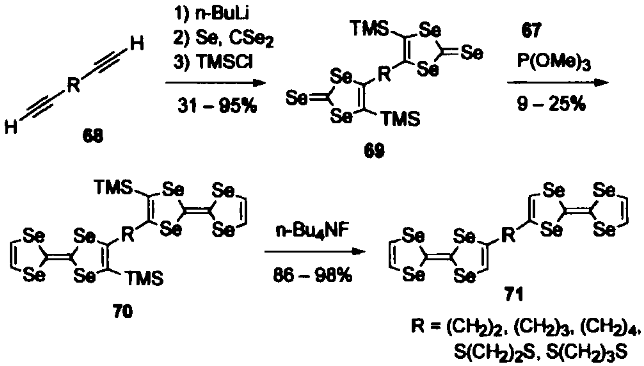
66



67

6. DIMERIC TSF DONORS

As one of the promising modifications of TTF, we recently developed the synthesis of dimeric TSFs (**71**) with an alkylene or alkylenedithio single spacer group.[28] These dimeric TSFs give an opportunity of controlling the stoichiometry and dimensionality of derived molecular complexes by intramolecular electronic interactions. As outlined in Scheme 18, these compounds were obtained via the key intermediates, bridged bis(1,3-diselenole-2-selones) (**69**), from the bis-diynes (**68**).

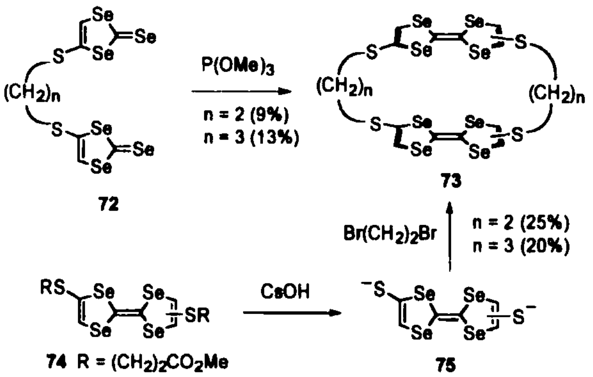


SCHEME 18

An X-ray crystallographic analysis of the dimeric TSF donors **71**, R = $(CH_2)_3$ revealed that in the neutral state, it adopts a stretched conformation, but a voltammetric analysis suggested that in the oxidized state, it favors a folded U-shape conformation. In addition, the UV-vis spectrum of the chemically oxidized species confirmed the formation of a π-dimer with U-shape conformation.

7. DOUBLE-BRIDGED TSF PHANES

Among dimeric TTFs, tetrathiafulvalenophanes (TTF phanes) are of current interest, because in such sophisticated systems, the two TTF units can adopt a unique sandwich structure so as to interact strongly with each other.[29] We previously found that the double-bridged TTF phanes especially behave as good electron donors forming highly conductive radical cation salts, and the high conductivities are induced by strong intra- and inter-molecular nonbonded interactions of the sulfur atoms incorporated in the TTF moieties.[30] In this regard, tetraselenafulvalenophanes (TSF phanes) should be more potential electron donors. The trimethyl phosphite-induced double-coupling reaction of the bis-1,3-diselenole-2-selones (**72**) gave a ready access to the double-bridged TSF phanes (**73**) (Scheme 19).[31] However, this double coupling reaction carried problems of low yield (9 – 13%) and poor reproducibility. An alternative synthetic method based on deprotection/realkylation of the protected TSF dithiolate provided an improved yield (20 - 25%) and high reproducibility.[32]



SCHEME 19

The Au(CN)$_2$ radical cation salt of TSF phane (**73**, n = 3) showed a high conductivity of 53 Scm^{-1}; its crystal structure includes stacked TSF phanes with the half-oxidized state on each TSF moiety and a sheet-like array comprising many intramolecular and intermolecular Se–Se contacts. This is a model example of the molecular complex with controlled stoichiometry and dimensionality derived from the dimeric TSF phane.

8. CONCLUDING REMARKS

This paper has described useful and versatile reactions that are applicable to the synthesis of new selenium- or tellurium-including TTF derivatives and demonstrated various examples, which further enrich TTF-type electron donors. In addition, it may be worth noting that the present synthetic methods have a potential of ready access to the building blocks of sophisticated multi-TTF systems, which attracted recent interest in TTF chemistry.

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